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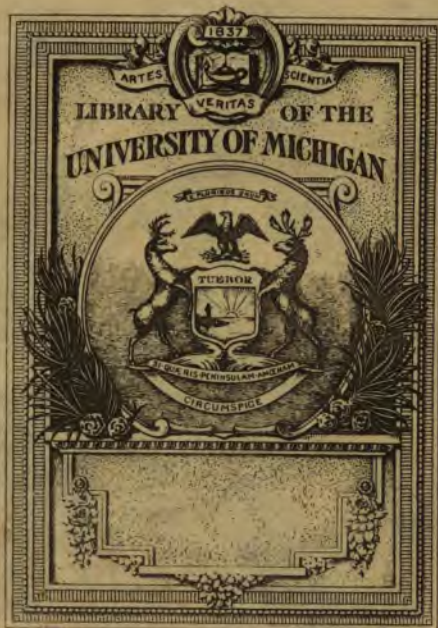
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THE GIFT OF  
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QD  
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1881

A MANUAL  
OF  
QUANTITATIVE CHEMICAL ANALYSIS

FOR THE USE OF STUDENTS.

BY

*signature*  
FREDERICK A. CAIRNS, A. M.,

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NEW EDITION, REVISED AND EDITED BY  
H. WALLER, Ph.D.,

INSTRUCTOR IN ANALYTICAL CHEMISTRY IN SCHOOL OF MINES.



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1881

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TO  
PROFESSOR CHARLES F. CHANDLER,  
THE FRIEND, TEACHER, AND CO-LABORER OF THE  
AUTHOR, THIS BOOK IS, IN ACCORDANCE  
WITH THE AUTHOR'S  
WISHES,  
DEDICATED.

## NOTE BY THE EDITOR.

---

Mr. F. A. Cairns, the author of this work, died suddenly while engaged in preparing the first edition for the press.

The undersigned completed what was found to be necessary, and the work was published.

After using it in class room and laboratory for a year, it has been deemed advisable to prepare and issue a new edition in which a few typographical errors have been corrected and some notes of an explanatory nature added. In a few cases it has also been found preferable to modify the phraseology employed, and a new chapter has been added on the testing of illuminating gas.

It is to be hoped that the changes made will meet with the approval of those making use of the book, and that the conscientious labors of the author will still have the cordial appreciation of workers in this branch of chemistry.

E. WALLER.

*Gift*  
*Mrs. N. M. Langdon*  
*12-13-27*

## AUTHOR'S PREFACE.

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This little manual is designed to assist beginners in the practice of quantitative analytical chemistry.

The aim is, by explaining some of the more serious obstacles to successful analysis, to teach thoughtfulness and caution, and by giving very explicit directions in the earlier part of the course, to induce habits of precision, and impart a sufficient amount of knowledge of chemical manipulation to enable the student to proceed without further leading.

The system adopted is to teach at first the determination, individually, of the constituents of compounds, composed of elements which will afterward, very frequently, be found variously associated, particularly in mineral analysis; and then to teach the quantitative separation of these elements, in the analysis of compounds containing a number of them; advancing, step by step, from the analysis of compounds of similar character to the analysis of more complicated ones, involving a knowledge and application of what has preceded.

In addition to the series of what may be called strictly mineral, have been added a number of analyses of substances of an organic character, found in commerce, which will give the student an insight into the work which will probably be required of him as a practical chemist.

The range of these is necessarily restricted, as it is desired to keep the work within the limits of a simple hand-book.

The writer has avoided giving numerous methods of analysis of the same substance, but has selected those which he knows to be good, and which he believes to be the best.

The instructor is expected to enlarge upon the instructions given here, and the student to study other works of a more elaborate character. Success requires knowledge of theoretical chemistry and quantitative analysis.

## REFERENCES.

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The references are to :

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## INTRODUCTION.

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As gravimetric analysis is effected by separating, one by one, the different constituents from a solution containing a known amount of the substance to be analyzed by adding other substances, called reagents, which will form with the constituents to be determined compounds insoluble in the surrounding fluid, care must be taken not to use excessive quantities of these reagents.

Take, as an illustration, the analysis of limestone. After decomposing the stone and separating the silica, which is done in acid solution, the solution is made alkaline with ammonia, by which means the ferric and aluminic hydrates, being insoluble in ammonia, are precipitated; the lime is then precipitated, by the addition of ammonium oxalate, as calcium oxalate, a compound insoluble in ammonia; the magnesia is then precipitated from the residual fluid as magnesium ammonium phosphate (by the addition of sodium phosphate), a compound insoluble in ammonia.

This is the outline of the method of analysis. Suppose an excessive quantity of hydrochloric acid to have been used in the first instance, a large quantity of ammonia would be required to precipitate the iron and alumina, and consequently a large quantity of ammonium chloride formed in the solution. If, in addition to this, an unnecessary quantity of ammonium oxalate were used, it would be found impossible to complete the analysis successfully.

without danger of loss and great waste of time and labor. The danger of loss always accompanies prolonged operations in chemistry; the waste of time would be consequent upon the necessity of evaporating to dryness to expel the large amount of ammonium chloride, in the presence of which the magnesium could not be completely precipitated (an operation involving considerable loss of time and possibly of substance). Finally, after all this waste of time and labor, the presence of other salts, not volatilized by heat, would render it impossible to concentrate the fluid to the proper point for the thorough precipitation of the magnesium as phosphate, it being somewhat soluble in large amounts of fluid. Such difficulties as these can in nearly all cases be avoided by using no more of a solvent (acid or alkaline) than is necessary, and no more of a precipitant than is required to effect complete precipitation, or, in other words, by avoiding excessive use of reagents in all cases.

A knowledge of the use of solvents can be attained by studying the solubility of substances, and a knowledge of the amount of reagents to be used by simple stoichiometrical calculations. The student should bear in mind that water is also a reagent, and that excessive use of it is to be condemned. At the end of this chapter will be found a table giving the amount of the different elements, etc., precipitated by 1 c. c. of a solution of each of the reagents most commonly used.

Before beginning an analysis of any complexity, a plan should be adopted and well studied. In many cases, tabular schemes will be found very useful, as they enable the chemist to see at a glance the relative bearing of each part of an analysis, and refresh the memory without loss of time.

#### MEASURING.

This requires vessels of various kinds, the capacity of which is known, such as flasks, pipettes, burettes, etc.

**Flasks.**—Of these it is well to have a series which will deliver respectively 50 c. c., 100 c. c., 150 c. c., 200 c. c., 250 c. c., 300 c. c., 500 c. c., and 1000 c. c. In most cases, it is not of so much importance that they should be absolutely accurate as to capacity, as that they should bear an accurate relationship to each other, as otherwise it will be impossible to divide solutions correctly, a matter of the greatest importance in quantitative analysis. If it is desired to standardize a flask with great precision, it can be done by counterpoising it on a balance with any kind of weight that is convenient, adding weights to those on the balance to an amount corresponding to the capacity of the flask, adding the proper amount of water, and marking the neck of the flask. As an illustration, we will suppose that it is desired to prepare a 50 c. c. flask. Select a flask with a narrow neck, in which the water will rise about half-way, upon introducing about 50 c. c. of it; dry the flask thoroughly, inside and out, place it upon the pan of a balance, counterpoise it with any convenient weight, add to the weight 49.9405 gms., and introduce into the flask distilled water of 16° C., until perfect equilibrium is produced (after drying the neck of the flask above the water-line). Then mark the neck of the flask, which must stand perfectly level, where it is intersected by the horizontal plane coinciding with the bottom of the meniscus. This mark is what is called the "holding" or "containing" mark. Of course, when the contents of the flask are poured out, some of the fluid will adhere to the sides, and it will fail to deliver 50 c. c. It becomes necessary, therefore, to establish a point to which the flask must be filled to enable it to deliver 50 c. c. To do this, fill the flask with water, empty it, counterpoise it as before, together with the fluid adhering to the inside, being careful that the outside is dry, replace the weights amounting to 49.9405 gms., introduce distilled water of 16° C. until equilibrium is restored as before, and mark the neck of the flask where it is intersected by the horizontal plane tangent to the bottom of the

meniscus. This mark is what is called the "delivery" mark.

In this way, all the flasks required can be prepared with great accuracy. If, however, an accurately measured flask is at hand, another of twice or thrice the capacity can readily be prepared by filling the smaller flask to the delivery mark with water of  $16^{\circ}$  C., emptying it into the larger flask, previously dried, repeating until the desired volume is reached, and marking upon the neck of the flask the holding point. By repeating the operation upon the wet flask, the delivery mark can be established.

Flasks can also be prepared with great ease by means of a pipette the capacity of which is known. If, for instance, a pipette which is known to deliver 50 c. c. is at hand, all that is necessary to prepare a 200 c. c. flask is to dry it, run into it 4 pipette-fulls of water of  $16^{\circ}$  C., and mark the proper point on the neck as the holding mark; and determine the delivery mark by repeating on the wet flask.

**Pipettes.**—These can usually be purchased cheaply, so that ordinarily there is no occasion to make or graduate them. Their accuracy should, however, always be verified. This is commonly done by filling them up to the proper mark with water of  $16^{\circ}$  C., running this water into a weighed flask, and weighing the amount delivered. This should be nearly the same number of grammes as the pipette is supposed to contain in cubic centimetres, a slight difference being made for the expansion of water between 0 and  $16^{\circ}$  C. One cubic centimetre of water at  $16^{\circ}$  C. weighs 0.9988 gms.

A pipette must always be filled by suction to above the mark, with the liquid to be measured; then, by closing the top with the dry finger, the liquid may be allowed to run slowly out, until the lower part of the meniscus is at the line. It will then (if correct) deliver the number of c. c. marked upon it. Pipettes being used for *delivery only*, have no holding mark, as with flasks. In running the liquid out of the pipette, touch the tip lightly against the

side of the vessel into which it is delivering, until no more runs out. Never blow out the last drop, since that renders the measurement inaccurate.

If a burette is taken, the accuracy of which has been verified by weighing the amounts delivered, as referred to above, the accuracy of any number of pipettes may be readily tested, by first filling them with water, running it out so as to leave the same amount adhering to the glass as when in use, and then closing the tip with the finger, and running in water of 16° C. from the burette. For this work, the burette should be provided with a fine-pointed delivery-jet.

The same method will serve for graduation, if that is necessary. (See Thorpe's "Quant. Anal." pp. 112 *et seq.*) Students should also have a few small test glasses holding from 10 to 15 c. c., and graduated to c. c. These will be found more convenient for controlling the use of reagents than pipettes, and for most purposes are sufficiently accurate.

For measuring of gases, read Fresenius, who extracts from the best authorities, such as Bunsen, Regnault, and others.

#### WEIGHING.

As quantitative analysis requires, in addition to the separation of the constituents of a substance, the determination of their relative quantity, accurate weighing is absolutely necessary. A good balance is, of course, essential. For discussions of the principles of the balance, the student is referred to such works as that of Fresenius, as space will not allow their being introduced here. Rules for weighing are all that are admissible. Those given by Fresenius are introduced here.

1. The safest and most expeditious way of ascertaining the exact weight of a substance is to avoid trying weights at random; instead of this, a strictly systematic course ought to be pursued in counterpoising substances on the

balance. Suppose, for instance, we want to weigh a crucible, the weight of which subsequently turns out to be 6.627 gms. ; we place 10 gms. on the other scale against it, and we find this too much ; we place the weight next in succession, *i. e.*, 5 gms., and find this too little ; next 7, too much ; 6, too little ; 6.5, too little ; 6.7, too much ; 6.6, too little ; 6.65, too much ; 6.62, too little ; 6.63, too much ; 6.625, too little ; 6.627, right.

I have selected here, for the sake of illustration, a most complicated case ; but I can assure the student of quantitative analysis that this systematic way of laying on the weights will, in most instances, lead to the desired end in half the time required when weights are tried at random. After a little practice, a few minutes will suffice to ascertain the weight of a substance to within the tenth of a milligramme, provided the balance does not oscillate too slowly.

2. The milligrammes and fractions of milligrammes are determined by a centigramme rider (to be placed on or between the divisions on the beam) far more expeditiously and conveniently than by the use of the weights themselves, and at the same time with equal accuracy.

3. Particular care and attention should be bestowed on entering the weights in the book. The best way is to write down the weights first by reference to the blanks or gaps in the weight-box, and to control the entry subsequently by removing the weights from the scale, and replacing them in their respective compartments in the box. The student should, from the commencement, make it a rule to enter the number to be deducted in the lower line ; thus, in the upper line, the weight of the crucible + the substance ; in the lower line, the weight of the empty crucible.

4. The balance ought to be arrested every time any change is contemplated, such as removing weights, substituting one weight for another, etc., etc., or it will soon be spoiled.

5. Substances (except, perhaps, pieces of metal, or some other bodies of the kind) must never be placed directly upon the scales, but ought to be weighed in appropriate vessels of platinum, silver, glass, porcelain, etc., never on paper or card, since these, being liable to attract moisture, are apt to alter in weight. The most common method is to weigh, in the first instance, the vessel by itself, and to introduce subsequently the substance into it; to weigh again, and subtract the former weight from the latter. In many instances, and more especially where several portions of the same substance are to be weighed, the united weight of the vessel and of its contents is first ascertained; a portion of the contents is then shaken out, and the vessel weighed again, the loss of weight expresses the amount of the portion taken out of the vessel.

6. Substances liable to attract moisture from the air must be weighed invariably in closed vessels (in covered crucibles, for instance, or between two watch-glasses, or in a closed glass tube); fluids are to be weighed in small bottles with glass stoppers.

7. A vessel ought never to be weighed while warm, since it will in that case invariably weigh lighter than it really is. This is owing to two circumstances. In the first place, every body condenses upon its surface a certain amount of air and moisture, the quantity of which depends upon the temperature and hygroscopic state of air, and likewise on its own temperature. Now, suppose a crucible has been weighed cold at the commencement of the operation, and is subsequently weighed again while hot, together with the substance it contains, and the weight of which we wish to determine. If we subtract, for this purpose, the weight of the cold crucible, ascertained in the former instance, from the weight found in the latter, we shall subtract too much, and consequently we shall set down less than the real weight of the substance. In the second place, bodies at a high temperature are constantly communicating heat to the air immediately around them; the

heated air expands and ascends, and the denser and colder air, flowing toward the space which the former leaves, produces a current which tends to raise the scale-pan, making it thus appear lighter than it really is.

#### FILTERING AND BEAKERS, ETC., WASHING.

Lipped beakers are always preferable. In pouring from a beaker, the stream should be always poured against a glass rod. No grease is required on the under side of the lip, if it is properly formed. The under side of the lip should always be dry. Rubbers on the rods should only be used to clean vessels. In filtering, the rods should have no rubbers on them, as it may introduce organic matter into the solutions, which may cause error in the work.

When a vessel holding several litres is to be heated, as it may be fractured by the great weight of fluid, if the bottom rests unevenly upon its support in heating, sand may be used as a support. In other cases, the use of sand is objectionable. It requires a longer time to heat a vessel standing upon sand, and the sand is very liable to adhere to the bottom of the vessel, and from it drop into the analysis.

In filtering, the filter should always be accurately fitted to the funnel, and the funnel adapted to the size of the filter, always using the smallest filter that will allow a proper washing of the contents. The larger the filter, the more washing it requires, and the greater the liability to error in allowing for the weight of the ash.

Corrugated filters should never be used in quantitative work, where the precipitate is to be weighed, as it is very difficult to wash them properly, and it is very difficult to remove the precipitate from them, which is often necessary.

In washing, allow all the solution to run through the



filter, before adding any water, then fill up the filter with water, and allow that to run through before adding more. By this means, excessive quantities of wash-water may be avoided. In washing by decantation, which is necessary with some precipitates, the same principle is used. Allow the precipitate to settle, decant as closely as possible, pouring the liquid through the filter, add water, stir well, let settle, and decant again closely before adding more wash-water.

**Crucibles and Ignition.**—Crucibles should always have covers, and be cooled and weighed with them on, to avoid loss of substance and to exclude dust, etc.

Previous to ignition, the filters and contents must be thoroughly dried; on ignition, the paper must be thoroughly consumed, so that no carbon remains. Heat gently at first, so as to carbonize the filter without flame, and afterward intensely. The destruction of the filter-paper is most readily effected by tilting the crucible, and finishing the ignition with the cover off. It is best to remove the contents from the filter so far as possible, before igniting. In many cases, the removal of any of the contents is impossible. In such cases, roll up the filter and contents, and burn both together. If the substance is one which may be reduced by the carbon of the filter-paper (as lead sulphate, etc.), moisten with a little concentrated nitric acid or strong solution of ammonium nitrate before igniting. Where the most of the precipitate can be removed from the filter without loss, it is better to do so, and reserve the precipitate in a watch-glass or convex cover, until the filter-paper has been consumed.

Where substances readily reducible are to be weighed, which might form a fusible alloy with platinum (lead sulphate, silver chloride, etc.), porcelain crucibles should be used.

**Note-Books.**—Notes should never be kept on loose scraps of paper, but in regular note-books, of a size sufficient to allow of keeping a clear record of the work, for reference

at any time. It is convenient to get in the habit of setting down the weight of the vessel in which a substance is to be weighed, in the lower line of the two intended for that purpose. In the case given below, the glass for the iron wire and the crucible for the precipitate are always weighed first, but the weight is entered on the lower line of the two, for convenience in subtracting.

As an illustration of a clear and convenient form of keeping a note-book, an example is given. The analysis is supposed to be the determination of iron in iron wire:

Wt. glass + Fe wire.....	6.0765
“ “ .....	5.8000
Fe wire taken.....	0.7765
Wt. Crucible + ignited ppt., etc.....	25.5170
“ “ .....	24.4059
“ ppt. + ash.....	1.1121
“ filter-ash.....	0.0081
“ ignited ppt.....	1.1090

*Calculation :*

$$1.1090 \times \frac{112}{160} = 0.7763 \text{ Fe}$$

$$0.7763 \times \frac{100}{0.7765} = 99.97 \text{ per cent Fe.}$$

#### MAKING UP REAGENTS.

In making up reagents, pure materials and distilled water should be used. In the table below, where salts are mentioned, the crystallized salts (containing water of crystallization) are meant. Salts obtained from dealers, and labelled ‘chemically pure,’ are seldom absolutely so, and often afford a sediment when their solutions are allowed to stand. Tests should always be made for such impurities as may interfere with the work. In some cases, the amount

# MAKING UP REAGENTS.

11

of impurity may have to be determined, and an allowance made for it in the work.

	Reagent.	Proportions to be used.	1 c. c. of solution will precipitate:	
$\text{BaCl}_2 + 2\text{H}_2\text{O}$	Barium Chloride	1 gm. salt 10 c. c. water	0.0327 gm. $\text{SO}_4$	7.15
$\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$	Hydrodisodic Phosphate....	" " " 10 c. c. "	0.0112 " $\text{MgO}$	7.17
$\text{C}_2\text{O}_4\text{H}^{2-} + 2\text{H}^+$	Ammonium Oxalate.....	" " " 24 c. c. "	0.0145 " $\text{CaO}$	7.20
$\text{AgNO}_3$	Argentive Nitrate	" " " 20 c. c. "	0.0104 " $\text{Cl}$	14
$\text{H}_2\text{SO}_4$	Sulphuric Acid..	1 gm. conc. (gr. 1.84) 5 c. c. "	0.2522 " $\text{Ba}$	
	" "	1 c. c. " " 5 c. c. " dilute	0.4291 " $\text{Ba}$	
$\text{Pt} + \text{Cl}_2$	Platinic Chloride.	1 gm. metal dissolved in aqua regia, evaporated to dryness and dissolved in 1 c. c. $\text{HCl}$ + 9 c. c. water.	0.0390 " $\text{K}$ 0.0480 " $\text{K}_2\text{O}$ 0.0750 " $\text{KCl}$	7.28
	Magnesia mixture, vid. Fres. Quant. § 62, p. 89.	1 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (salt), 1 gm. $\text{NH}_4\text{Cl}$ (salt), 4 c. c. ammonia, 8 c. c. water.	0.0240 " $\text{P}_2\text{O}_5$	7.3
	Molybdate solution, vid. Fres. Qual. § 55, p. 72.	1 gm. $\text{MoO}_3$ dissolved in 4 c. c. ammonia, poured into 15 c. c. $\text{HNO}_3$ (gr. 1.2).	0.0018 " $\text{P}_2\text{O}_5$	7.81
$(\text{NH}_4)_2\text{C}_2\text{O}_6 + 3\text{H}_2\text{O}$	Ammonium Carbonate, 1 gm. salt, 1 c. c. ammonia, 4 c. c. water.			
$\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$	Sodium Carbonate, 2.7 gm. salt, 5 c. c. water. (Saturated solution.)			1.5
$\text{NH}_3$	Ammonia, gr. 0.96.*			
$\text{HCl}$	Hydrochloric Acid, gr. 1.12.			
$\text{HNO}_3$	Nitric Acid, gr. 1.2.			

\* The strongest concentrated ammonia has a gr. of 0.880. This, diluted with two volumes of water, will have a gravity of 0.96.

$\text{Ba(NO}_3)_2$	Baric Nitrate	
$\text{JH}^+\text{Cl}$	Aqua Regia	1 part $\text{HNO}_3$ to 3 or 4 parts $\text{HCl}$
$\text{KNO}_3$	Ammonie Chloride	1 part $\text{NH}_4^+$ to 5 parts Nitric
$\text{Na}_2\text{H}_2\text{O}_7 + 3\text{H}_2\text{O}$	Potassic Permanganate	10 grms $\text{O}_2$ $\text{KNO}_3$ in 1 liter Water
	Sodic Acetate	
	Kiesser	
	Calc. Sulph.	
	Calc. Chloride	
	Kiesel S.	
	Ammonium Sol.	

7.2  
7.5  
7.9  
17.9

## CHAPTER I.

### BARIUM CHLORIDE.



The composition of crystallized barium chloride is:

Ba.....	56.147 per cent.
Cl.....	29.099 " "
H <sub>2</sub> O.....	14.754 " "
	<hr/> 100.000

Pulverize 8 or 10 gms., and keep the powder in a corked tube or bottle. For the determination of the barium, dissolve 1 gm. in 100 c. c. warm water, containing a few drops of hydrochloric acid. Heat to boiling, and add 2 c. c. dilute sulphuric acid, prepared by adding 1 part by volume of strong acid to 5 parts by volume of water. Continue boiling for 1 minute. Then remove the heat, and allow the precipitate of barium sulphate to settle completely.

To determine whether or not a sufficient quantity of sulphuric acid has been added, place 2 or 3 drops of the clear supernatant fluid on a watch-glass, and add a drop of barium chloride solution. If, upon the addition of the barium chloride, the fluid becomes turbid, with a precipitate of barium sulphate, there is evidently a sufficient quantity of sulphuric acid present to precipitate all the barium in the solution. Should no turbidity appear after adding the barium chloride to the solution on the watch-glass, add 1 c. c. more of the dilute sulphuric acid to the main solution, boil, and test a few drops of the clear fluid, as before. Repeat the testing and addition of acid until the fluid evidently contains an excess. When the precipitation is complete, decant the clear fluid on a filter, without disturbing the precipitate, pour 100 c. c. boiling water on the precipitate, stir well with a glass rod, allow

the precipitate to settle, and decant as before. Repeat this washing by decantation several times. Then, transfer the precipitate to the filter, and wash with hot water until the wash-water does not become turbid when either barium chloride or silver nitrate is added to it. After filtering out the barium sulphate and washing by decantation, and before transferring the precipitate to the filter, substitute a clean empty beaker for the one containing the filtrate, in order that an unnecessary amount of re-filtering may be avoided, should the precipitate of barium sulphate run through the filter, which sometimes happens when the filter-paper is very thin. Dry the precipitate on the filter, and when it is dry brush it from the filter into a clock-glass or small dish as completely as possible; burn the filter in a weighed crucible, keeping the crucible covered until the paper is thoroughly charred. After this, remove the cover and continue to heat until the carbon of the paper is completely consumed and only white ash left. Then transfer the precipitate from the clock-glass to the crucible, ignite thoroughly, cool in a desiccator, and weigh. The weight will be that of the crucible, filter-ash, and precipitate of barium sulphate. Deduct the known weight of the crucible and filter-ash, and from the remainder, which will be the weight of the barium sulphate, calculate the per cent of barium.

The combustion of the filter can be hastened by pressing it against the side of the crucible, while burning, with a clean glass rod.

If the barium sulphate be not completely removed from the filter before burning it, a little may possibly be reduced to barium sulphide by the carbon of the filter. This danger may be avoided by moistening the filter-ash with two or three drops of sulphuric acid, drying, and igniting again, before transferring the precipitate to the crucible.

For the determination of the chlorine, dissolve 0.500 gm. of the pulverized barium chloride in a small conical part-

*By water solution*  
ing-flask, or matrass, such as is used in the assay of gold. Fill the flask about half full with warm water—warm to about 60° C., and add 16 c. c. of a solution of silver nitrate, prepared by dissolving 1 part by weight of pure silver nitrate in 20 parts of water, add 1 c. c. of nitric acid, cork the flask, and shake well. When the precipitate has settled, add 1 c. c. more of the solution of silver nitrate, and notice carefully whether or not it causes another precipitate. If it should do so, shake, and allow the silver chloride to settle, add another c. c. of the silver nitrate solution, and proceed in the same way until no new precipitate forms, and the solution “brightens,” as it is termed; that is, looks perfectly clear. Heat to 60° C. Allow the precipitate to settle completely, fill the flask with warm water, place over the mouth a weighed porcelain crucible of a proper size to allow the mouth of the flask to touch the bottom of it, and invert it quickly. Hang the flask by means of a wire triangle in a ring of an ordinary ring-stand, over an evaporating dish sufficiently large to hold more than the contents of the flask. Lower the ring until the crucible stands on the bottom of the dish, the crucible being all the time pressed firmly against the mouth of the flask. Fill the crucible with water and gently raise the ring, adding water while doing so, until the mouth of the flask is so slightly submerged that a watch-glass, a trifle larger than the crucible, can be slipped under it. Do not place the watch-glass under the mouth of the flask at first, but allow the whole to stand for some hours, protected as far as possible from the light.

The precipitate will usually settle entirely from the flask into the crucible; should any particles adhere to the sides of the flask, slight tapping will cause them to descend. After all the precipitate has settled into the crucible, slip the watch-glass under the mouth of the flask, and, while holding it firmly against it with one hand, remove the crucible containing the silver chloride with the other; allow the fluid in the flask to run out slowly

into the dish by moving the watch-glass gently with a rocking motion. Now pour the fluid in the crucible carefully into another vessel, or, for greater security, on a filter. Wash repeatedly with hot water, containing a little nitric acid, decanting on the filter as before, until the washings do not become turbid upon the addition of hydrochloric acid. In testing, use only a few drops at a time, in a very slender test-tube. Remove the last drops of fluid from the crucible with a strip of bibulous paper, being careful not to take up any silver chloride; should any particles adhere, they can be washed back into the crucible, and the fluid removed as before. By a little care and dexterity, all but a very small quantity of fluid can, in this way, be removed. Evaporate off what remains in the crucible, and then dry it, with its contents, in a drying chamber. When all visible moisture is removed, heat over a low flame, until the silver chloride begins to fuse well around the edge; cool and weigh. Deduct from this weight the known weight of the crucible. The remainder will be the weight of the silver chloride. From this, calculate the per cent of chlorine. The silver chloride should not be fused at a high heat, as it will volatilize some of it. This is the best method of determining chlorine gravimetrically, where a large quantity of silver chloride is to be handled.

The silver chloride can be precipitated in a beaker instead of a flask, and filtered out. Precipitate in the same way as directed above; pour the clear fluid on the filter, wash a few times by decantation with hot water acidulated with nitric acid, transfer the precipitate to the filter, and wash with hot water acidulated with nitric acid, until the washings do not become turbid upon the addition of hydrochloric acid, to be sure that the excess of silver nitrate is washed out. Dry the precipitate in the funnel in an air-bath. When the precipitate is dry, transfer it to a clock-glass, brushing the filter as clean as possible with a feather; place the filter in a weighed porcelain crucible, moisten it with a few drops of nitric acid, and burn it

until all carbon is consumed. Let the crucible cool enough to be handled, add a few drops of nitric acid, and warm, to dissolve the metallic silver which is due to the reduction of the silver chloride by the carbon of the filter. Then add a few drops of hydrochloric acid and evaporate to dryness. Transfer the precipitate from the clock-glass to the crucible, fuse as directed above, cool and weigh. The weight will be that of the crucible, filter-ash and silver chloride. Deduct the known weight of the crucible and ash of filter; the remainder will be the weight of the silver chloride. From this, calculate the per cent of chlorine.

Whichever method be employed, evaporate the filtrates and washings to small bulk, after adding a little silver nitrate and nitric acid. Should a precipitate of silver chloride be formed, treat it as directed above, and add the per cent to the first.

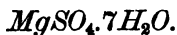
For the determination of water, introduce 1 gm. into a weighed crucible, and heat very gently to low redness; cool and weigh. Repeat the heating and weighing until the substance ceases to diminish in weight. Care should be taken not to heat too highly, as by doing so some chlorine may be expelled.

The loss of weight is equivalent to the water; from this, calculate the per cent of water.



## CHAPTER II.

### MAGNESIUM SULPHATE.



The theoretical composition of magnesium sulphate is :

MgO.....	16.26 per cent.
SO <sub>4</sub> .....	82.52 " "
H <sub>2</sub> O.....	51.22 " "
	<hr/> 100.00

As the salt is slightly efflorescent, select 8 or 10 gms. of crystals that have not lost water by exposure, pulverize them quickly, and keep the powder in a corked tube or bottle.

For the determination of magnesia, dissolve about 1 gm. in 25 c. c. of cold water in a small beaker, add enough hydrochloric acid to make the solution distinctly acid to test-paper, and then enough ammonia to make it decidedly alkaline. Should a precipitate of magnesium hydrate occur, make the solution acid again with hydrochloric acid, and then alkaline again with ammonia, as before. Repeat this treatment if necessary until ammonia no longer produces a precipitate. Allow the fluid to cool, and add 16 c. c. of a solution of hydro-disodium phosphate, prepared by dissolving 1 part by weight of the salt in 10 parts of water. Agitate the contents of the beaker well with a glass rod, being careful not to rub the sides of the vessel with the rod, as it will cause crystals of ammonia-magnesium phosphate to adhere to the glass so tenaciously as to be difficult to remove. Allow the solution to stand cold 12 hours, and, when the precipitate has entirely settled, place 3 or 4 drops of the clear fluid on a watch-glass, or in a very small test-tube, and add 2 or 3 drops of "magnesia mixture." If a precipitate forms, it shows that enough hydro-disodium phosphate has been used ; if no precipitate forms, add 5 c. c. of the precipitant to the main solution, and proceed as before. Filter on a very

*disodium phosphate solution*

small filter, and wash with dilute ammonia, prepared by mixing 1 part of strong ammonia with 2 parts of water, until no turbidity is produced by silver nitrate in 1 c. c. of the washings acidulated with nitric acid, or by barium chloride in the same quantity acidulated with hydrochloric acid. Dry the precipitate on the filter, and, when it is dry, brush it from the filter into a large watch-glass, and burn the filter in a weighed crucible. When the carbon of the filter is entirely consumed, transfer the precipitate to the crucible, and ignite again, increasing the heat to bright redness, keeping the crucible covered. Then remove the cover, and heat strongly, until the contents of the crucible are white, or nearly so. Should the contents of the crucible appear dark in color, moisten them with a few drops of nitric acid; evaporate off the excess of acid carefully, and ignite again, until the precipitate is of a light gray color. Cool the crucible and contents in a desiccator, and weigh. Deduct the known weights of the crucible and filter-ash. The remainder will be the weight of the magnesium pyro-phosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ). From this weight calculate the per cent of magnesia.

For the determination of the  $\text{SO}_3$ , dissolve 1 gm. in 100 c. c. warm water, acidulate slightly with hydrochloric acid, boil, add 12 c. c. of a solution of barium chloride—prepared by dissolving 1 part by weight of crystallized barium chloride in 10 parts of water—and continue the boiling for 2 or 3 minutes. Allow the precipitate to settle, and test a few drops of the clear fluid with sulphuric acid. If no precipitate is produced by the sulphuric acid, there cannot be an excess of barium chloride in the solution. In such a case, add another c. c. of barium chloride solution, stir, and allow the precipitate to settle, and test again. Proceed in the same way, until the appearance of a precipitate upon testing shows that there is a sufficient quantity of barium chloride present. Finally, allow the precipitate to settle, decant the clear fluid on a filter, pour on the precipitate 100 c. c. of boiling water containing 2 or 3

c. c. of hydrochloric acid, stir, allow the precipitate to settle, and again decant on the filter. Repeat this treatment, and then transfer the precipitate to the filter with hot water, and wash with the same until a few drops of the wash-water show no turbidity when treated with silver nitrate, and leave no more residue, when evaporated on platinum and ignited, than will be left by a similar quantity of distilled water, treated in the same way. Dry the precipitate, brush it on a clock-glass, burn the filter moistened with a few drops of sulphuric acid in a weighed crucible, add the precipitate, ignite strongly, cool, and weigh. Deduct the known weights of the crucible and filter-ash. The remainder will be the weight of the barium sulphate. From this calculate the per cent of  $\text{SO}_3$ .

As the precipitate of barium sulphate has a tendency to carry down with it barium chloride, which it is difficult to remove by washing, after igniting the precipitate, brush it from the crucible into a beaker, moisten with a few drops of hydrochloric acid, add water, and boil. Then transfer all to a filter, wash well, dry, ignite, and weigh. Where barium sulphate has been precipitated in a fluid containing salts of iron, it is nearly impossible to purify it in this manner. In such a case, fuse the ignited precipitate with a little sodium carbonate, digest the mass with boiling water until it is disintegrated, transfer it to a filter, and wash well. By this means, the barium will remain on the filter as carbonate, with the impurity, while the sulphuric acid will pass into the filtrate, from which it can be precipitated free from impurity.

For the determination of the water, introduce about 1 gm. of the salt into a weighed crucible, heat to redness, cool, and weigh. Again heat, cool, and weigh. Repeat until the crucible and contents no longer lose weight by being heated. The difference between the weights of the crucible and contents, before and after heating, is due to the loss of water. From this, calculate the per cent of water.

## CHAPTER III.

## CALCIUM CARBONATE.



The theoretical composition of calcite is :

CaO.....	56.00	per cent.
CO <sub>2</sub> .....	44.00	" "
	<hr/>	
	100.00	

For the determination of the lime, dissolve 1 gm. in 3 c. c. of strong hydrochloric acid, and 25 c. c. of boiling water. It should dissolve completely ; should it not, filter out any residue, and wash with about 50 c. c. of hot water. Then wash the residue from the filter into a very small beaker with as little water as possible, and add 2 c. c. of hydrochloric acid, and boil. Should it dissolve, add the solution to the first one ; should it not dissolve, pass the fluid through the same filter, wash, and add the filtrate to the first solution. The combined solutions should not amount to more than 200 c. c. Dry the insoluble residue, burn it in a weighed crucible, determine its weight from the original weight of substance. The difference expresses the actual weight of calcite taken for analysis. To the combined solutions add enough ammonia to make the fluid decidedly alkaline to test-paper, heat to boiling, and add 50 c. c. of ammonium oxalate solution, prepared by dissolving 1 part by weight of the salt in 24 parts of water. Boil hard for two or three minutes. Then remove the heat, allow the fluid to cool and the precipitate to settle. To be sure that enough ammonium oxalate has been used, put 3 or 4 drops of the clear fluid on a watch-glass or in a small test-tube, add 1 drop of ammonia and two or three drops of solution of calcium chloride. The formation of a precipitate proves that enough ammonium oxalate was used in the first instance. If no precipitate

Ammonium  
oxalate  
Solution

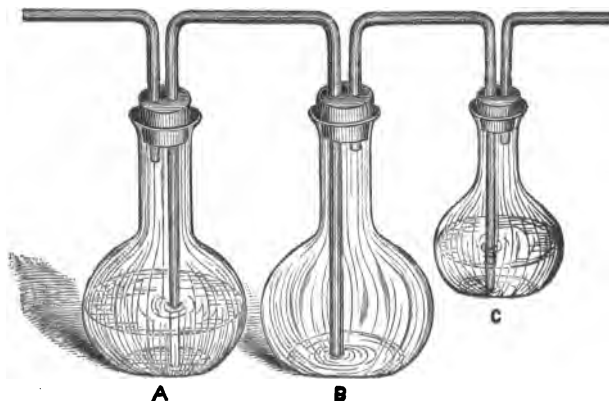
forms, add 10 c. c. more ammonium oxalate to the main solution, and test again in the same way. Proceed in this manner until assured that enough of the precipitant has been added. When the precipitate has thoroughly settled, decant the clear fluid on a filter, after pouring off as much of the fluid as possible. Without disturbing the precipitate, remove the beaker containing the filtrate, and place another under the funnel. Then transfer the precipitate to the filter with hot water, and wash it down into the point. More washing than will effect that object is unnecessary, as the impurities that may possibly be present, that is, ammonium chloride and oxalate will be expelled by the after-treatment of the calcium oxalate with sulphuric acid. The object aimed at in removing the beaker containing the filtrate is to avoid having to re-filter a large amount of fluid, should the precipitate of calcium oxalate run through the filter, as it sometimes does, particularly when the filter-paper is very thin. Remove any calcium oxalate adhering to the walls of the beaker with a feather or rubber. If any adhere so tenaciously as to render it impossible to remove it with a rubber, wash it off with a little dilute hydrochloric acid into a small beaker; add ammonia to alkaline reaction, a few drops of ammonium oxalate, and boil two or three minutes. When the precipitate has settled, filter through the same filter. The water required to transfer the precipitate to the filter will wash it sufficiently. Dry the filter and contents at a temperature not exceeding 100° C., to avoid making the filter brittle. When the precipitate is dry, brush it into a clock-glass, cleaning the filter as thoroughly as possible. Burn the filter in a weighed crucible until only white ash is left. Remove the heat, and when the crucible is cool, transfer the precipitate from the glass to the crucible, add enough strong pure sulphuric acid to moisten the precipitate, place the lid on the crucible and expel the excess of sulphuric acid by heating over a Bunsen burner, allowing the flame to touch only the lip

or edge of the crucible cover. After expelling all free sulphuric acid, ignite strongly for a few minutes, cool in a desiccator, and weigh. This weight, after deducting the known weights of crucible and filter-ash, will be that of calcium sulphate. From this calculate the per cent of lime.

The filter should be cleaned as thoroughly as possible, as ignition will convert any adhering calcium oxalate into calcium hydrate or carbonate which will effervesce violently upon the addition of sulphuric acid, thereby causing loss of substance, by projecting it from the crucible. The reaction between calcium oxalate and sulphuric acid takes place without any violent action.

The carbonic acid is determined by loss of weight of the substance after expelling the gas, or by weighing the gas after absorbing it in potassium hydrate, or soda-lime.

There are a great many kinds of apparatus devised by chemists for determining carbonic acid by loss. One which every one can prepare for himself, is constructed of 3 small flasks, *A*, *B*, and *C*, two of which, *A* and *B*, hold about 100 c. c. each, and the third, or *C*, about 25 c. c.



Each flask is provided with a doubly-perforated cork, or rubber stopper. Through the first hole of the stopper of flask *A* passes a piece of small glass tubing, about one

and a half inches long. Through the other hole, passes, nearly to the bottom of the flask, one limb of a glass tube bent twice at right angles, the other limb of which passes through the first hole of the stopper of the other 100 c. c. flask, *B*, nearly to the bottom. Through the other hole of the stopper of flask *B*, sufficiently far to clear the stopper, passes the short limb of a tube, bent twice at right angles, while the longer limb passes through the first hole of the stopper of the 25 c. c. flask, *C*, nearly to the bottom. Through the other hole, passes a short tube, about one and a half inches long. Into flask *A*, introduce 30 c. c. of dilute nitric acid; into flask *B*, a carefully-weighed quantity of the calcium carbonate (about 1 gm.), and into flask *C*, 10 c. c. of concentrated sulphuric acid. Put the apparatus together, and weigh. Then draw a little acid over from *A* into *B*, by sucking at the exit tube of *C*, and close the open tube of *A* by placing over it a short piece of rubber tubing, the other end of which is closed by a piece of glass rod. When the violent effervescence is over, open the closed tube of *A*, and repeat the operation, until enough acid is drawn from *A* into *B* to decompose the calcium carbonate. Then close the open tube of *A*, and raise the contents of the flask *B*, to incipient boiling. Then remove the heat; at the same time, remove the stopper from the open tube of *A*, attach in its place a small calcium-chloride tube, containing equal parts of calcium chloride and soda lime, and draw a gentle current of air through the apparatus by means of an aspirator. The air should not pass more rapidly than at the rate of 2 bubbles in a second, or the aspiration be continued longer than is necessary to clear the apparatus of carbonic acid. The passage of half a litre of air will effect this. The amount can be determined by the volume of water that escapes from the aspirator. The carbonic acid can be sucked out by the mouth. If this plan be adopted, the air should be drawn through until it no longer tastes of carbonic acid. After a sufficient volume of air has been drawn through the

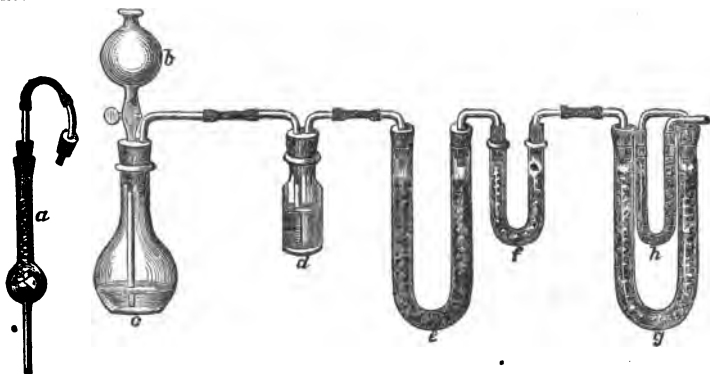
apparatus to extract the carbonic acid, allow the apparatus to cool, remove the aspirator, if one has been used, and the calcium-chloride tube from the open tube of flask A, and weigh. The difference between this and the first weight of the apparatus is equivalent to the weight of carbonic acid. In many cases, the determination of carbonic acid by loss is inadmissible. In such cases, it is absorbed in some substance with which it will combine, as potassium hydrate or soda-lime. For this purpose, an apparatus such as that described by Fresenius in his work on Quantitative Analysis (§ 139 e p. 293), under the head of carbonic acid, can be used. In making the determination, do not use more than 0.500 gm. of calcium carbonate, as a large quantity necessitates the use of large absorption tubes. If soda-lime be used, it is well not to use the tube after more than one half of the contents have been heated by the carbonic acid.

For the analysis, weigh the absorption tubes, introduce the weighed substance into the decomposing flask, put the apparatus together, close the stop-cock of the funnel-tube, and attach the aspirator. After the aspirator has drawn long enough to produce a partial vacuum in the apparatus, introduce about 30 c. c. of dilute nitric acid, through the funnel-tube, into the decomposing-flask. As soon as all the acid is in, close the funnel-tube. After the first violent effervescence has ceased, apply gentle heat to the flask, and gradually increase it, until the fluid in the flask begins to boil. Then remove the heat, attach the guard tube, containing soda lime and calcium chloride, open the stop-cock or clamp, and draw air through the apparatus, very slowly, until the absorption tubes are cool, or until about 2 litres of air have passed through. When the tubes are cool, weigh them. The difference between this weight and the first weight of the tubes is equivalent to the carbonic acid. The carbonic acid can also be determined by introducing a weighed quantity into a tube of hard glass, by means of a small platinum



boat, and igniting strongly, at the same time, drawing through the tube a current of dried air. Attach to the tube a weighed tube, filled with neutral calcium chloride, over which carbon dioxide has been passed for some time. This will absorb the water, and allow the carbonic acid to pass. After the carbonic acid is expelled from the substance, weigh both the boat and contents, and also the calcium-chloride tube. The loss of weight of the boat will be carbonic acid plus water, while the increase of weight of the calcium-chloride tube will be water. The difference between the weight of carbonic acid and water, determined by loss, and the weight of water will be that of carbonic acid. Not more than 0.500 gm. of substance should be used.

NOTE.—The apparatus used in the estimation of the carbonic acid is represented below.

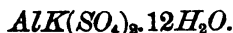


*a* contains soda-lime; it can be attached to *b* with a cork. *b* is provided with a glass tap. The flask *c* has a capacity of 200 c. c. *d* contains sulphuric acid. *e* contains pumice saturated with sulphuric acid. *f* contains pumice which has been saturated with solution of sulphate of copper, and then heated strongly till all the water has been expelled. *g* contains soda-lime and *h* sulphuric acid on pumice. The pumice used in this apparatus should be previously heated with strong sulphuric acid, washed and dried, as it is liable to contain chlorides and fluorides. The loose sulphuric acid in the U tubes should not rise above the bend when at rest.

*g* and *h* are the only pair in the train which are weighed. They should be provided with rubber tubes, stopped with glass rod to prevent absorption of carbonic acid or moisture from the air.

## CHAPTER IV.

### POTASSIUM ALUM.



The theoretical composition of potassium alum is :

Al <sub>2</sub> O <sub>3</sub> .....	10.86 per cent.
K <sub>2</sub> O.....	9.90 " "
SO <sub>3</sub> .....	83.72 " "
H <sub>2</sub> O.....	45.52 " "
	<hr/>
	100.00

Pulverize 5 or 6 gms. coarsely and quickly, and keep the powder in a small corked bottle, or specimen tube. For the determination of alumina, first weigh the tube, and contents; then shake out a little into a beaker, and again weigh the tube, and remaining substance. The diminution in weight, of course, shows the amount taken. Proceed in this way until about 1 gm. has been transferred to the beaker. Pour upon it 100 c. c. of hot water and stir; when all is dissolved, add 2 or 3 c. c. of strong hydrochloric acid, and enough ammonia to turn red test-paper blue, and emit a slight odor of ammonia. Be cautious not to add a large excess, or time will be wasted in boiling it out, which will be necessary for the reason that aluminum hydrate is somewhat soluble in excess of ammonia. Boil until the vapors no longer smell of ammonia, and do not turn turmeric paper brown. Allow the precipitate to settle, and decant the clear fluid on a filter. Then pour 40 or 50 c. c. of boiling water on the precipitate, stir, allow it to settle, and decant the clear fluid on the filter as before. Repeat this treatment several times, and finally transfer the precipitate to the filter, with boiling water, and wash with the same, until a few drops of the wash-water, acidulated with nitric acid, do not show a precipitate of silver chloride when treated with

a drop of silver nitrate, or a precipitate of barium sulphate when treated with hydrochloric acid and barium chloride. It is unnecessary to begin washing on the filter until about 100 c. c. have passed through the filter. Test the filtrate and washings with litmus paper. If they are not alkaline, add ammonia until the fluid is faintly alkaline, and heat. Should a precipitate appear, filter it out, wash, dry it, and reserve it to be burned with the other. When the main precipitate is perfectly dry, ignite it, with the smaller one, should there be any, rolled up in the filter, in a weighed crucible furnished with a lid, applying the heat gently at first, and then intensely, in order to expel any adhering sulphuric acid. During the latter part of the ignition remove the cover from the crucible, in order thoroughly to consume the filter. When the filter is completely burned, remove the heat, cool and weigh. This weight, after deducting the weight of the crucible and filter-ash, will be the weight of the alumina.

For the determination of  $\text{SO}_3$  concentrate the filtrate from the alumina to 200 c. c. by evaporation, add hydrochloric acid until the fluid is slightly acid, and then add 12 c. c. of barium chloride solution, prepared by dissolving 1 part by weight of crystallized barium chloride in 10 parts of water. Boil for a few minutes and allow the precipitate of barium sulphate to settle, and proceed as directed in the analysis of magnesium sulphate. Observe the precautions there given, as to washing and purification of the precipitate.

To determine the potassium, add ammonia to the filtrate from the barium sulphate until it is slightly alkaline, heat to boiling, and add ammonium carbonate as long as it produces a precipitate of barium carbonate. When all the barium is precipitated, decant the clear fluid on a filter, wash by decantation 3 or 4 times, using about 50 c. c. of hot water each time, transfer the precipitate to the filter, and wash it well with hot water, or until 2 or 3 drops of the wash-water, acidified with nitric acid, show

*Barium  
Chloride  
Solution*

no cloudiness when treated with silver nitrate. Pour 3 or 4 funnelfuls through the filter before beginning to test. When all the potassium chloride is washed out, evaporate the filtrate and washings to dryness in a platinum dish, and ignite to faint redness, until all the ammonium chloride is expelled. This may be ascertained by holding over the vessel a clean cold clock-glass. The non-appearance of a white coating on the glass indicates the absence of ammonium chloride. Dissolve the residue in about 25 c. c. of warm water, filter the solution into a small porcelain dish, and wash with hot water, testing the wash-water with silver nitrate, as directed above, to be sure that all potassium chloride is washed out. When the filter and contents are sufficiently washed, add to the fluid 2 drops of concentrated hydrochloric acid and 8 c. c. of platinum tetrachloride solution, prepared by dissolving 1 part by weight of platinum tetrachloride in 10 parts of water, and evaporate to a pasty consistency, on a water-bath. Then pour into the dish about 50 c. c. of alcohol, of about 85 per cent, without removing the dish from the bath, and heat for two or three minutes. Then wash the contents of the dish into a small flask, marked *A*, with alcohol of 85 per cent, and cork it immediately, to avoid the possibility of absorption of ammonia from the air of the laboratory, of which there is frequently great danger. After the potassium platino-chloride has entirely settled, and the fluid shows by its color that a sufficient amount of platinum tetrachloride has been added, pour off the clear fluid into another flask, marked *B*, as completely as possible without transferring any of the precipitate, cork it, and allow it to stand long enough for any particles of potassium platino-chloride, which may have passed over with the fluid from flask *A*, to subside. Then pour into the first flask, *A*, 20 or 30 c. c. of 85 per cent alcohol, cork it, and after agitating it gently set it aside, until the contents of the flask *B* are disposed of. Pour the contents of *B* into a dish, add about 10 c. c. of water, and proceed to evapo-

rate off the alcohol on a water-bath. Should there be any particles of the precipitate in the fluid, first pour off as much as possible into the dish, without disturbing the precipitate, and evaporate it as above, and pour the rest, with the precipitate, on a filter. Add this filtrate to the fluid already evaporating. Keep the funnel covered with a glass while filtering. After all the fluid has thus been transferred to the dish for evaporation, pour upon the same filter the contents of flask A, washing the precipitate into the filter with 85 per cent alcohol. Dry the filter and contents in an air-bath at 100° C. Ignite the dry precipitate, rolled up in the filter, in a weighed crucible, applying the heat very gently at first, and keeping the crucible covered until the filter-paper is charred. Then remove the cover from the crucible, and ignite at a higher degree of heat, until the filter is entirely consumed. Allow the crucible to cool, add a little oxalic acid, heat gently at first, until the water of crystallization of the oxalic acid is expelled, and then more intensely until the acid is decomposed, and all the carbon consumed. Cool the crucible, and wash by decantation with hot water as long as the wash-water becomes turbid from formation of silver chloride, when treated with silver nitrate. By this means, the double chloride is decomposed, and all the potassium and chlorine washed out, leaving only spongy platinum. Heat alone fails to decompose the compound completely.

After the platinum is sufficiently washed, dry the crucible and contents, and ignite until every thing is consumed but spongy platinum. Cool, and weigh. Deduct from this weight, that of the crucible and filter-ash. The remainder will be the weight of platinum. From this, calculate the per cent of potassium or of potassium oxide.

After all the alcohol has been expelled from the original filtrate by evaporation, as directed above, add 1 c. c. of platinum tetrachloride solution, and a very small quantity of pure sodium chloride; continue the evaporation to

pasty consistency, treat with alcohol, and proceed as directed for the treatment of the main precipitate. Should any more potassium platino-chloride be obtained, treat it as above, and add the per cent to that of the main precipitate. The sodium chloride tends to prevent the decomposition of the platinum chloride, while evaporating the alcoholic solution.

Instead of igniting the dry precipitate of potassium platino-chloride, it may be weighed as such. In this case, filter through an exhausted filter; that is, one which has been previously washed with hydrochloric acid, and then with water until all the acid is removed from the paper. Then dry the filter between watch-glasses, held together by a clip. After weighing the glasses, clip, and paper together, previously dried at  $100^{\circ}$  C., transfer the filter to a funnel, and filter the solution through it. Dry the filter and precipitate first in the funnel at  $100^{\circ}$  C. Then place them between the glasses, secure the glasses by means of the clip, dry again at  $100^{\circ}$  C., cool, and weigh. The increase in weight will be that of the precipitate of potassium platino-chloride. From this, calculate the per cent of potassium. This method is tedious and objectionable where a small quantity of potassium platino-chloride is to be dealt with. If great care is exercised in preparing and drying the filter, it may be adopted where a large amount of potassium is to be determined.

For the determination of water, weigh about 1 gm. shaken from the tube, as directed above, into a weighed crucible, heat to  $250^{\circ}$  C., cool, and weigh. Repeat the heating and weighing until the substance ceases to lose weight. The loss of weight is equivalent to the weight of water expelled. From this, calculate the per cent of water.

## CHAPTER V.

### CALCIUM FLUORIDE.



The theoretical composition is :

Ca.....	51.28	per cent.
Fl.....	48.72	“ “
	<hr/>	
	100.00	

Introduce into a weighed platinum crucible 1 gm. of the finely-powdered mineral, mix it, by means of a coarse platinum wire, with pure concentrated sulphuric acid, to the consistence of paste ; add enough more acid to make the mixture semi-fluid, place the crucible with the cover on, in an inclined position on a support, and heat with a Bunsen burner, allowing the flame to strike the edge of the crucible and lid. Continue heating until all the sulphuric acid is expelled, and the calcium converted into sulphate, cool, weigh, and calculate the weight of calcium. The difference between the weight of calcium and the weight of mineral taken is equivalent to the weight of fluorine expelled. From these data, calculate the per cent of calcium and fluorine.

There are various methods for determining fluorine, varying in complexity with the character of the substances treated. It was suggested by Berzelius (Rose, p. 883) to distill the fluoride of silicon from substances that could be decomposed by sulphuric acid, by heating with this acid, adding powdered silica if necessary, in a retort of lead or platinum, delivering into a vessel of water. The acid used must be pure and concentrated, the silica pure and in the form of very fine powder, and the metallic tube connected with the retort must dip into mercury just far enough to prevent the point from coming in contact with

the water, or the separated silica will clog it. The fluoride of silicon, when it comes in contact with the water, is decomposed into silica, which separates, and hydro-flu-silicic acid, which goes into solution. Filter out the silica, wash it well, dry, and weigh it. To the acid fluid containing hydro-fluosilicic acid, Rose (*lb.* p. 883) adds potassium chloride and alcohol. The potassium silico-fluoride is collected on a weighed filter, washed with dilute alcohol, consisting of equal parts of alcohol and water, dried at 100° C., and weighed. The fluorine calculated from the silica, and from the precipitate of potassium silico-fluoride, will together give the per cent in the substance.



To determine the fluorine in substances insoluble in water, and not decomposable by acid, Berzelius (*Vid. Fres. Quant.*, § 166a) fused the substance with 4 parts of sodium carbonate at a strong red heat, digested the mass in water, boiled, filtered, and washed, first with boiling water, then with a solution of ammonium carbonate. The filtrate will contain all the fluorine as sodium fluoride, together with carbonate, silicate, and aluminate of sodium. The filtrate is to be mixed with ammonium carbonate, and the mixture heated, the ammonium carbonate which evaporates being replaced. The aluminium hydrate and silicic acid is then filtered off and washed with ammonium carbonate. The filtrate is then heated until the ammonium carbonate is completely expelled, and the fluorine determined. Rose suggests a modification of Berzelius's treatment after reaching this point, which is as follows: Add a solution of calcium chloride as long as a precipitate continues to form. When the precipitate, which consists of calcium fluoride, and calcium carbonate, has subsided, it is washed, first by decantations, afterward on the filter, and dried. When dry, it is ignited in a platinum crucible. Water is then



poured over it, in a platinum or porcelain dish, acetic acid added in slight excess, the mixture evaporated to dryness on a water-bath, and heated on the latter until all odor of acetic acid disappears. The residue, which consists of calcium fluoride and calcium acetate, is heated with water, the calcium fluoride filtered off, washed, dried, ignited, and weighed. If the precipitate of calcium fluoride and calcium carbonate were treated with acetic acid, without previous heating, the washing of the fluoride would be very difficult. From the weight of the calcium fluoride, calculate the per cent of fluorine.

See H. Rose, *Anal. Chem.*, chapter on Fluorine, p. 757.

## CHAPTER VI.

### POTASSIUM IODIDE.

#### *KI.*

The theoretical composition is :

K.....	23.545 per cent.
I.....	76.455 “ “
	<hr/> 100.000

To determine the potassium, dissolve 1 gm. of the salt in about 10 c. c. of water, in a small porcelain dish, add 2 or 3 c. c. strong nitric acid, and evaporate to dryness on the water-bath, to expel the iodine. It may be necessary to repeat this operation in order to drive out the last traces of the iodine. Take up with about 20 c. c. of water, add 1 c. c. strong hydrochloric acid, and proceed as directed in the analysis of potassium alum.

To determine the iodine, weigh carefully 0.250 gm. of the salt, transfer it to a parting flask, add warm water, an excess of silver nitrate and nitric acid, and proceed as directed in the analysis of barium chloride, for the determination of chlorine, care being taken to add excess of silver nitrate before adding the nitric acid.

The iodine can also be determined with great accuracy by precipitating it, as palladium iodide, in a solution of the salt, slightly acidified with hydrochloric acid, warming gently and allowing the whole to stand for about 24 hours, to give the precipitate ample time to form and settle. It is better finally to ignite the precipitate, and from the metallic palladium calculate the iodine.

See Fres., § 145—1—b, p. 311, and H. Rose, chapter on Iodine, p. 824.

## CHAPTER VII.

### POTASSIUM BROMIDE.

#### *KBr.*

The theoretical composition of the salt is :

K.....	32.835 per cent.
Br.....	67.165 " "
	<hr/>
	100.000

For the determination of the potassium, proceed exactly as in the previous analysis of potassium iodide, or boil with dilute chlorine water until the bromine is expelled, and then proceed.

The bromine is determined as silver bromide, in the same manner as chlorine is determined as silver chloride, in the analysis of barium chloride.

See H. Rose, *Anal. Chem.*, chapter on Bromine, p. 815.

## CHAPTER VIII.

### HYDRO-DISODIUM PHOSPHATE.



The theoretical composition of hydro-disodium phosphate is :

Na <sub>2</sub> O.....	17.32 per cent.
P <sub>2</sub> O <sub>5</sub> .....	19.83 " "
H <sub>2</sub> O.....	62.85 " "
	<hr/> 100.00

Select 4 or 5 gms. of the crystals which have lost no water by efflorescence, break them up quickly into a coarse powder, and keep the powder in a small, well-corked bottle or large specimen tube, and weigh the portions required for analysis as directed in the case of potassium alum.

Perhaps a better plan is to dissolve about 5 gms. in 100 c. c. of water, transfer the solution to a 250 c. c. flask, dilute to the holding mark, and mix the fluid well by pouring several times from the flask into a beaker and back. Then draw from the flask with a pipette the quantity required for analysis, and cork the flask to prevent evaporation of the fluid.

For the determination of sodium, dissolve about 1 gm. of the salt in about 50 c. c. of water, or take an equivalent amount from the solution of a large quantity. Then dissolve about 0.600 gm. piano-forte wire in 80 c. c. dilute hydrochloric acid, add 3 c. c. of strong nitric acid, and boil. Then concentrate the solution until nearly all free acid is expelled, dilute with 10 c. c. of water, and add the solution to that of the sodium phosphate. To the combined solutions add ammonia in excess, and heat to boiling. Then remove the heat, and allow the precipitate to settle. When the precipitate has settled thoroughly,

and the supernatant fluid become colorless, filter off the clear fluid, and wash the precipitate three or four times, using 50 or 60 c. c. of hot water each time. Then transfer the precipitate to the filter, and wash again with hot water, until the washings show only a slight opalescence upon addition of silver nitrate and nitric acid. In testing the washings, use only 2 or 3 drops each time. The precipitate will contain all the phosphoric acid, combined with the ferric oxide, and may be rejected. Evaporate the filtrate and washings to dryness on a water-bath. Just before the point of dryness is reached, add dilute hydrochloric acid, little by little, until the fluid is slightly acid to test-paper. By delaying the addition of the acid until nearly all the ammonia is expelled by the evaporation, there will be less ammonium chloride to burn out, and less danger of loss of sodium chloride by ignition. Continue the evaporation, and, when the mass is perfectly dry, ignite gently until vapor of ammonium chloride ceases to be evolved. Cool, dissolve in a little boiling water, and filter into a weighed platinum dish; washing the filter until a few drops of the wash-water do not give a precipitate of silver chloride, when treated with silver nitrate. Then evaporate the filtrate to dryness, ignite gently, and weigh the sodium chloride. From this weight, calculate the per cent of soda. The ignited sodium chloride should be white and perfectly soluble in water. If it is not, filter the solution, wash the insoluble residue, evaporate the filtrate and washings to dryness, ignite, and weigh again.

For the determination of phosphoric acid, take 1 gm. of the salt, weighed as directed in the analysis of potassium alum, or a portion of a solution of larger quantity equivalent to 1 gm. If 1 gm. of the solid salt is taken, dissolve it in 50 c. c. of cold water, acidify the solution with hydrochloric acid, and then make it slightly alkaline with ammonia. When the solution is cool, add 12 c. c. of "magnesia mixture," and set it aside for some hours. The "magnesia mixture" is prepared by dissolving 1 part by

*p*  
*magnesia mixture*  
*W.D.*

weight of crystallized magnesium sulphate and 1 part by weight of ammonium chloride in 8 parts of water and 4 parts of ammonia. After the precipitate of ammonio-magnesium-phosphate has entirely settled, filter, wash with dilute ammonia until the washings give no reaction for sulphuric acid, and place the funnel containing the precipitate in an air-bath to dry. Reserve the filtrate for some hours. Should another precipitate appear, filter it out on the smallest-sized filter, wash it with 20 or 30 c. c. of dilute ammonia, dissolve it through the filter with a little dilute hydrochloric acid into a small beaker, and make the solution alkaline with ammonia. If the ammonia produces a precipitate, filter it out, wash it with dilute ammonia, dry, and ignite with the main precipitate of ammonio-magnesium-phosphate. Ignition converts this into magnesium pyrophosphate. From this, after weighing and deducting the weight of the crucible and filter-ash, calculate the per cent of  $P_2O_5$ . It sometimes happens that, in precipitation of phosphoric acid by means of magnesia mixture, some magnesium hydrate is precipitated with the phosphate. When there is reason to suspect that such has been the case, from the flocculent appearance of the precipitate, dissolve the ignited precipitate of pyrophosphate in a little hydrochloric acid, dilute slightly, add a few drops of nitric acid, and boil gently for about an hour, renewing the fluid from time to time. By this means, the pyrophosphoric acid will be converted into the tribasic acid again. Then make the fluid alkaline with ammonia. The ammonio-magnesium-phosphate will be precipitated free from magnesium hydrate, and is to be treated as directed above. It is necessary to convert the pyrophosphoric or tetrabasic into the tribasic acid before adding the ammonia, as the pyrophosphate is soluble to an appreciable extent in ammonia water.

For the determination of the water, weigh 1 gm. of the phosphate in a boat made of platinum foil. Introduce the boat into a tube of hard glass about 8 or 10 inches long,

such as is used for combustion in organic analysis. One end of this tube is closed by a cork, through which passes a short piece of smaller glass tubing, while the other end is drawn out to a long point, bent at a right angle to the body of the tube. Insert the point into an ordinary calcium chloride tube previously filled and weighed, letting it project a short distance through the cork. This arrangement is designed to afford an uninterrupted passage of the water from the ignition-tube into the calcium chloride, and allow the application of heat very near the extreme point of the ignition-tube, to drive all the water into the absorption-tube containing anhydrous calcium chloride. Connect the cork for the other end of the ignition-tube by means of rubber with another tube containing calcium chloride. This latter is intended to dry the air drawn through the apparatus. After the boat containing the substance is introduced into the ignition-tube, insert the cork, attach the weighed absorption-tube to the point, connect the other end of the absorption-tube by means of rubber tubing with an aspirator, and proceed to draw a gentle current of air through the apparatus. Then apply heat to the ignition-tube sufficient to expel the water. When this is all drawn into the absorption-tube detach the aspirator, allow the apparatus to cool, and weigh the absorption-tube. The increase in weight will be equivalent to the weight of water. From this, calculate the percent as usual.

## CHAPTER IX.

### AMMONIO-FERRIC SULPHATE, OR AMMONIA IRON ALUM.



The theoretical composition of the salt is:

Fe <sub>2</sub> O <sub>3</sub> .....	16.60 per cent.
SO <sub>3</sub> .....	33.20 " "
NH <sub>3</sub> .....	3.52 " "
H <sub>2</sub> O.....	46.68 " "
	100.00

Select 8 or 10 gms. of crystals which have not lost water by efflorescence; break them into small pieces or coarse powder, and keep for analysis in a small, well-corked bottle. Consult analysis of hydro-disodium phosphate.

For the determination of the ferric oxide by precipitation, take as nearly as possible 1 gm. weighed in the manner directed in the analysis of potassium alum, or an equivalent amount from the solution of a larger quantity, if the plan suggested in the analysis of hydro-disodium phosphate be adopted.

If 1 gm. of the solid salt be weighed, dissolve it in 100 c. c. hot water and 1 c. c. dilute hydrochloric acid. When the solution is complete, add ammonia (little by little) until the fluid is slightly alkaline, and heat to boiling. Then remove the heat and allow the precipitate to settle; decant the clear fluid through a filter, pour upon the precipitate 50 c. c. hot water, stir, allow the precipitate to settle, and pour the clear fluid through the filter as before. Repeat this washing by decantation three times. Then transfer the precipitate to the filter with hot water, and wash with hot water until the washings give no precipitate when treated with barium chloride solution. Dry the precipitate thoroughly, and remove it from the filter



by inverting the latter on a clock-glass, and rubbing the filter between the fingers. By this means, nearly all of the precipitate can be removed from the filter, without any danger of loss by brushing. After removing the precipitate as cleanly as possible, burn the filter in a weighed crucible, after adding a few drops of nitric acid. When the carbon of the filter is completely consumed, brush the precipitate into the crucible, and ignite again, keeping it covered until all danger of decrepitation is past. Then remove the cover, and heat to a bright red heat. After heating intensely for some minutes, remove the heat, cool the crucible and contents in a desiccator, and weigh. From this weight, we obtain the per cent of  $\text{Fe}_2\text{O}_3$  by deducting the weight of crucible and filter-ash. If the contents of the crucible should look black, moisten with a few drops of nitric acid, evaporate off the excess of acid carefully, ignite, cool, and weigh again.

For the determination of the  $\text{SO}_3$  acidulate the filtrate from the ferric hydrate, and proceed as in the analysis of magnesium sulphate.

To determine the ferric oxide by ignition, introduce about 1 gm. of the salt into a previously-weighed crucible, and heat gently, and then gradually increase the heat to the highest point attainable over a blast-lamp. Cool and weigh. Repeat until the weight becomes constant. The expulsion of the sulphuric acid can be facilitated by introducing into the crucible a piece of pure ammonium carbonate about the size of a pea, covering the crucible, and heating moderately until the ammonium carbonate is volatilized, and then strongly, as before. Only ferric oxide will be left. Calculate the per cent as usual.

Of the various methods suggested for the determination of iron volumetrically, it is unnecessary to notice more than two, namely, that turning upon the use of potassium permanganate, and that in which potassium bichromate is employed.

The first method, known as Marguerite's, depends upon

the fact that a solution of potassium permanganate, which is intensely colored, loses its color when dropped into a solution of ferrous oxide, giving up a portion of its oxygen, and being decomposed into salts of manganese and potassium, until the ferrous is completely converted into ferric oxide. The moment this conversion is complete, the permanganate imparts color to the fluid.

The analysis requires a standard solution of potassium permanganate, that is, one the value of which is known.

To prepare this solution, dissolve 6.500 gms. of pure crystals of potassium permanganate in 1 litre of distilled water, with frequent agitation to insure complete solution, if possible. After this, allow the fluid to stand for 24 hours, and siphon off into another vessel the perfectly clear solution, and close this tightly with a stopper, preferably of glass.

There are several methods of standardizing the solution of potassium permanganate. Of these, only two will be described as reliable, namely, by means of iron, or by oxalic acid. Of these, the former (the method proposed by Marguerite) is the better one. Use for the purpose fine piano-forte wire, which contains 99.7 per cent of iron. Dissolve 0.200 gm. of the wire—previously cleaned with sand-paper to remove oxide, glaze, and dirt—in a small valved flask, with 25 or 30 c. c. of dilute sulphuric acid, by the aid of gentle heat; introducing into the flask, with the wire, a small crystal of sodium carbonate, about as large as a hemp-seed; by which means the atmospheric air will be displaced by carbonic acid, thus preventing the formation of ferric oxide during the solution. When the iron is dissolved, allow the flask and contents to cool slowly. Do not attempt to hurry the cooling by the application of any cold substance, as the sudden formation of a partial vacuum may crush the flask and scatter the contents.

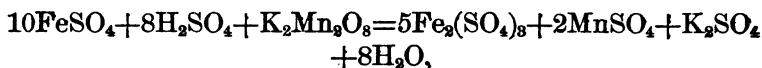
A very convenient kind of valve for the flask in which the iron wire is dissolved is the Kroonig valve, described

by Mohr in his *Titrimethode* (5th ed., 1877, p. 182), which is made of a piece of thick rubber tubing, about one and a half inches long, one end of which is forced over a short glass tube, passing through the cork into the neck of the flask, while the other end is closed by a short piece of glass rod. The rubber tube has a longitudinal slit cut in it between the end of the piece of glass rod and the glass tube. When the pressure is internal, the slit opens, allowing the gas and vapor to escape, and it closes when the pressure is external, owing to the cooling of the flask, thus preventing the entrance of oxygen.

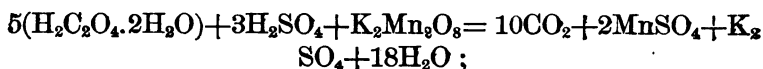
When the contents of the flask are cool, empty them into a large beaker, wash the flask well, adding the washings to the solution, and dilute with distilled water to about 700 c. c. Then drop in the solution of potassium permanganate to be standardized, slowly, from a Gay-Lussac burette, with constant stirring, until the color (which disappears rapidly at first, and then more gradually) finally becomes permanent, and remains so for one minute. The final color should be a light pink. Note carefully the quantity of potassium permanganate used, and calculate the value of 1 c. c. thus: Suppose 19.2 c. c. of the permanganate solution to be sufficient to oxidize the solution of 0.200 gm. of iron wire, or 0.1994 gm. of pure metallic iron (as the wire is assumed to contain 99.7 per cent of the latter); consequently, 1 c. c. of the permanganate solution will represent 0.01038 gm. of metallic iron, or 0.01483 gm. of ferric oxide. (Fres., *Quant.*, § 112, p. 194.)

To standardize the potassium permanganate solution by means of oxalic acid, dissolve 6.300 gms. of pure crystallized oxalic acid in 1 litre of water. Take 50 c. c. of the solution, equivalent to 0.315 gm., and dilute with about 100 c. c. of water. Add 6 or 8 c. c. pure concentrated sulphuric acid, and heat to about 60° C. Add permanganate solution from a Gay-Lussac burette, until it imparts a permanent color, as directed in the previous method.

By comparing the equations representing the reactions, it will be seen that the same quantity of potassium permanganate is required to oxidize 1 molecule of oxalic acid, whose molecular weight is 126, or 2 atoms of iron (in the form of monoxide), whose molecular weight is 112. Thus, the following represents the oxidation of iron,



while the next one represents the oxidation of oxalic acid,



consequently,  $126 : 112 = 0.315 : 0.280$ . In other words, the 0.315 gm. of crystallized oxalic acid contained in the 50 c. c. of solution taken as directed above, represents 0.280 gm. of metallic iron; and the quantity of permanganate solution required to oxidize 0.315 gm. of oxalic acid will oxidize 0.280 gm. of metallic iron. Suppose 27 c. c. of the permanganate solution to be required to oxidize the 0.315 gm. of oxalic acid, then 1 c. c. will be equivalent to 0.01037 gm. of metallic iron, or the result of dividing 0.280 by 27. The objection to the use of oxalic acid for standardizing potassium permanganate is the uncertainty of procuring a perfectly normal acid.

Whichever method of standardizing the permanganate solution is adopted, it is necessary to make more than one trial. Should the quantities of permanganate required in two trials not differ by more than one tenth of a cubic centimetre, the average of the two may be taken as correct. Should a greater difference than this occur, more trials must be made to obtain consistent results.

To determine the ferric oxide, weigh about 4 gms. of the ammonio-ferric sulphate, observing the precautions suggested before, transfer the substance to a flask holding 500 c. c., add about 200 c. c. of warm water and 2 or 3 c. c. of sulphuric acid. When all is dissolved, cool, and dilute

with cool water to the holding mark. Pour the solution into a dry beaker, and stir well. Divide the fluid into two equal portions, by filling a dry 250 c. c. flask with a portion of it, to the holding mark, emptying the flask into a reducing bottle, washing the flask, and adding the wash-water to the other. If the flasks agree, one half will have been transferred to the bottle; and that remaining in the beaker, together with that adhering to the larger flask, will compose the other half. This, with the washings of the beaker and flask, is to be transferred to another reducing bottle of similar size. Place in each of the bottles a piece of amalgamated zinc, and a piece of platinum foil about three quarters of an inch wide and four inches long, fill with water to the shoulders, cover with watch-glasses, and allow to stand for 24 hours. A strong current of gas should be induced by contact between the zinc and platinum. When the foil is new, it sometimes fails to produce the desired effect. In such a case, heat it in a strong solution of potassium hydrate, to remove oily matter; scour the surface with coarse sand, to roughen it, and wash it. Should the foil still act badly, wet the surface with a little nitro-hydrochloric acid, to remove the polished surface, and wash it with water. The zinc used should be amalgamated; otherwise, as it usually contains iron, in dissolving, it will impart iron to the solution. It has been found by experiment that amalgamated zinc will not give up the iron alloyed with it, to the solution to be reduced, until nearly, if not quite, all the zinc is dissolved.

A very good bottle for reducing the ferric oxide is about two and a half inches wide, and six inches high, with a wide mouth.

After the ferric is reduced to ferrous oxide, empty one of the bottles into a large beaker, wash it well with water, adding the washings to the solution; add 2 or 3 c. c. pure sulphuric acid, dilute to about 700 c. c., and titrate with the permanganate solution in the same manner as directed

for standardizing. The number of c. c. of potassium permanganate used, multiplied by the standard, gives the weight of metallic iron in the solution treated. From this, calculate the per cent of ferric oxide.

The two titrations should not differ more than two tenths of a c. c. If they do, another determination should be made.

*Potassium Bichromate Solution*

The other method of determining iron volumetrically, by the use of potassium bichromate, is preferable when the iron is in hydrochloric acid solution. The following equation,  $6\text{FeCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 3\text{Fe}_2\text{Cl}_6 + 2\text{KCl} + \text{Cr}_2\text{Cl}_6 + 7\text{H}_2\text{O}$ , shows that 1 eq., or 295.18 parts of potassium bichromate, will convert 6 eq., or 336 parts of iron, to the ferric state. Then, if 14.759 gms. of potassium bichromate are dissolved in 1 litre of water, 1 c. c. of the solution will be equivalent to 0.0168 gm. of iron. Before using the potassium bichromate, it should be fused, and cooled under a desiccator. The solution of bichromate should be standardized with piano-forte wire, as directed before for potassium permanganate, dissolving 0.200 gm. in 30 c. c. of dilute hydrochloric acid. After the solution is cool, pour it into a beaker, dilute, and drop in from a burette the bichromate solution, constantly stirring with a glass rod. The solution will soon turn green. Should it turn brown, add more hydrochloric acid. When it becomes dark green, place a drop on a white plate, and combine it with a drop of solution of potassium ferricyanide, which will turn it blue. *or ferricyanide* The solution of potassium ferricyanide should not be too strong, or it will give a red precipitate. As the oxidation by the potassium bichromate advances, the blue color produced by the solution of iron will become faint. Note the number of c. c. of bichromate solution used, and finish with one only one tenth as strong. When the tests no longer produce a blue color, the oxidation is complete. From the number of c. c. used calculate what 1 c. c. is equivalent to.

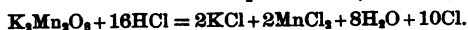
For the analysis, reduce the hydrochloric acid solution

of the salt with zinc and platinum, as directed before, titre with the bichromate solution, and from the number of c. c. used, and the known value of 1 c. c., calculate the iron.

For the determination of the ammonia, weigh about 1 gm. of the substance, and introduce it into a small tubulated retort, the tubulure of which is fitted with a tight caoutchouc stopper, through which passes a funnel tube, provided with a stop-cock. The kind called "thistle tube" is the best. The neck of the retort is connected with a piece of glass tube, of about the same size, and about 10 inches long, by means of a short piece of large rubber tube, stretched over both, and firmly tied. The glass tube is previously contracted by heat at the end nearest the retort, and filled with clean broken glass. The other end is fitted with a caoutchouc stopper, through which passes a small glass tube, turned down, so as to enter a small flask holding about 200 c. c., and passing through the stopper nearly to the bottom of the flask. This tube has blown on it a large bulb, to prevent recession of the fluid from the flask into the retort, in case of sudden contraction of the contents of the latter. Through the stopper of the flask also passes the point of an ordinary calcium chloride tube, filled with broken glass. Connect the apparatus, fasten the retort in a holder, with the neck inclined slightly upward, at the same time supporting the tube connected with it and filled with clean broken glass, and run into the flask, through the calcium chloride tube, enough dilute hydrochloric acid, of about 1.050 sp. gr. to slightly cover the point of the tube connecting the flask with the retort. Then introduce into the retort, through the funnel tube, enough water to dissolve the ammonio-ferric sulphate. When this is dissolved, run in through the funnel tube 20 or 30 c. c. of a concentrated solution of potassium hydrate, little by little. Then close the stop-cock and apply gentle heat, gradually increasing it, until the fluid in the retort boils. Continue

the boiling for 15 or 20 minutes. When the ammonia is expelled, open the stop-cock of the funnel-tube, and draw a little air through the apparatus. Then disconnect it, wash the tube connecting the flask with the large tube attached to the retort into a small porcelain dish, and at the same time run water through the calcium tube into the flask, and pour the contents into the dish, washing the flask well. Add to the contents of the dish an excess of platinum tetrachloride, and proceed as directed in the analysis of potassium alum. Great caution must be exercised in igniting the ammonium platino-chloride, or loss will be incurred by fine particles of platinum being carried off by the ammonium chloride. Rose directs that the covered crucible be subjected to a low heat for a long time, until the filter is completely charred, and that then a gradually-increasing heat be applied to the uncovered crucible, resting on its side, with the lid resting against the mouth. The fusion with oxalic acid, and the accompanying washing, are not required in this case, as the double chloride is easily decomposed and reduced to spongy platinum by heat alone. From the weight of spongy platinum, calculate the per cent of  $\text{NH}_3$ .

NOTE.—In determining iron by Marguerite's method, the presence of  $\text{HCl}$  must be avoided, especially if the solution is at all warm, since the permanganate under these circumstances will react upon the  $\text{HCl}$ , affording chlorine. Thus :



Some of the chlorine may convert the ferrous salt present into the ferric, but some will usually escape, and the results obtained will consequently be higher than the truth.



## CHAPTER X.

### FELDSPAR.

The following analyses, taken from Dana's *Mineralogy* show the composition of ordinary feldspar :

	Orthoclase.	Albite.
Silica.....	64.25	65.46
Alumina.....	18.80	20.74
Ferrous Oxide.....		0.54
Lime.....	1.20	0.71
Magnesia.....		0.74
Soda.....	2.40	9.98
Potash.....	12.44	1.80
Loss by ignition.....	0.80	.....
	99.39	99.97

Pulverize 3 or 4 gms. of the feldspar very fine, in an agate mortar, and keep the powder in a small, corked bottle. Fuse over a blast-lamp 1 gm. of this, carefully weighed, in a 2-oz. platinum crucible, intimately mixed with about 5 gms. of flux, composed of equal parts of potassium and sodium carbonates. The combined carbonates make a much more fusible flux than either alone. Examine the crucible occasionally, and, when the contents are fused so to flow when the crucible is inclined, move it about, after laying the cover aside in a convenient place, in such a way as to cause the contents to coat the sides, instead of cooling in a solid mass at the bottom, and dip it, while still hot, into a beaker of cold water, to about half of its depth. Hold it in the water for a few seconds, remove it, and, after the lapse of a few more seconds, dip it again. Repeat this treatment until the crucible and contents are cool enough to immerse without spattering. Then lay the crucible on its side in the beaker, which should be just large enough to permit this, and have in it

a sufficient quantity of water barely to cover the crucible. Then put the lid also in the beaker, and, after placing a convex glass over it, allow it to stand until the fused mass is sufficiently softened to be removed from the crucible. Owing to the contraction and expansion caused by this treatment, the mass can frequently be removed at once from the crucible in thin cakes. The object of using as small a beaker and as little water as possible is to avoid the evaporation, afterward, of an unnecessary quantity of fluid. Should the contents of the crucible be difficult to remove in this way, the operation may be hastened by digesting on a water-bath, occasionally moving the crucible with a glass rod, and replacing the water lost by evaporation. Under no circumstances should an effort be made to remove the mass by force, as in doing so there is great danger of injuring the crucible. After removing the substance from the crucible, place the latter, with the cover, in another vessel, pour on them a little dilute hydrochloric acid, to dissolve any adhering particles, and wash them with water. Pour this solution cautiously into the vessel containing the fused feldspar, keeping it covered with a glass, to prevent loss by effervescence, and add more hydrochloric acid, if necessary, a little at a time. When the fluid is acid, heat until all carbonic acid is expelled. Then, if the mineral is entirely decomposed, transfer all to a casserole, and evaporate on a water-bath to dryness. Then heat in an air-bath at a temperature of from  $100^{\circ}$  to  $110^{\circ}$  C. until the odor of hydrochloric acid disappears. Should there be any undecomposed mineral, allow it to settle, decant the clear fluid into a casserole, and begin to evaporate it as above. In the mean time, add some strong hydrochloric acid to the residue, and heat to dissolve it if possible. Should it dissolve, add the solution to the first one. Should it not dissolve, dilute with a little water, filter, wash, and add the filtrate to the principal solution. Dry the insoluble residue, burn it with the filter in a platinum crucible, fuse it with about five

times its weight of mixed carbonates, as in the first case, and treat as directed above. Repeat the treatment until the feldspar is all decomposed. Undecomposed mineral can be detected by the rapidity with which it settles to the bottom of the fluid, and by feeling hard and gritty when pressed by a glass rod, while separated silica rises readily in the solution when agitated, settles slowly, and offers no resistance to the rod. After the mass is thoroughly dried, moisten it with 20 c. c. dilute hydrochloric acid, heat at a temperature just below boiling for 20 or 30 minutes, and dilute with 50 c. c. hot water; every thing should now be in solution except the silica. Now filter out the silica, wash it with hot water until the washings give no reaction for chlorine, when treated with silver nitrate, and dry the precipitate on the filter, at a temperature of from 100° to 110° C. When the silica is perfectly dry, invert the filter in a weighed platinum crucible, standing on a sheet of glazed paper, roll the filter gently between the fingers in such a way as to remove the contents from the paper to the crucible, and, without lifting the filter from the crucible, fold it and press it carefully down upon the silica. After brushing into the crucible any particles that may have fallen on the paper, put on the cover, and ignite at first at a heat not more than sufficient to char the paper. Continue the low heat as long as smoke emerges from the crucible. After all volatile matter has been expelled, incline the crucible on the support, and gradually raise the heat to the highest point attainable by means of a good burner, keeping the cover on for a few minutes. Finally, remove the cover, and continue heating until the carbon of the filter is consumed and the silica is white. Then cool the crucible and contents in a desiccator, weigh, and calculate the per cent of silica, which still retains, perhaps, a little alumina. After weighing, moisten the contents of the crucible with pure concentrated sulphuric acid, add about 1 gm. of ammonium fluoride, which leaves no residue after ignition, incline the

crucible on the support, replace the cover, and apply the heat of a burner in such a way that the flame will strike the edge of the crucible and lid. When the sulphuric acid is expelled, heat the whole crucible strongly, cool, and weigh it. Repeat this treatment until the crucible ceases to lose weight. The loss represents silica expelled as silicon fluoride. If any thing remains in the crucible, fuse it with a little acid potassium, or sodium sulphate, cool, moisten with sulphuric acid, and heat again, until the mass becomes fluid. Finally, cool and dissolve in water, and add the solution to the filtrate from the silica.

Rapid ignition in the first instance, will cause loss of silica, as its particles, being very minute and light, are liable to be carried off by the gases expelled from the filter-paper by combustion, and also by the vapor of the water remaining in the silica itself after drying, since all moisture can not be expelled from it by drying at a temperature which will not destroy the fibre of the filter.

To determine the alumina, add to the filtrate from the silica, ammonia until the fluid is slightly alkaline, and proceed as directed in the analysis of potassium alum.

If there be any oxide of iron in the feldspar, it will be found in the precipitate of alumina, in which case fuse the ignited precipitate with pure potassium hydrate, preferably in a silver crucible, digest the fused mass until it is reduced to a pulverized form, and entirely removed from the crucible, which is to be washed and removed. Digest again, until the alumina is dissolved in the alkaline fluid, and only ferric hydrate remains. Filter, wash well, dry, ignite, and weigh the ferric oxide. Its weight, deducted from the known weight of alumina and ferric oxide combined, gives the weight of the alumina; or the alumina may be determined directly by acidifying the alkaline solution with hydrochloric acid, then making it alkaline with ammonia, boiling, and determining the alumina as before, as directed in the analysis of potassium alum.

To determine the ferric oxide by titration, fuse the ignited precipitate of alumina containing ferric oxide, with 6 or 8 times its weight of acid potassium sulphate, until the second molecule of sulphuric acid is expelled; cool, add a volume of pure concentrated sulphuric acid equal to that of the fused mass, heat again carefully, until the contents of the crucible become fluid. Then cool, place the crucible in a vessel of hot water, and digest over heat until the sulphates are dissolved. Then reduce with zinc and platinum, and titrate with potassium permanganate, as directed in the analysis of ammonio-ferric sulphate, and calculate the per cent of ferric oxide. If this method is adopted, the alumina is, of course, to be determined by difference.

To determine the lime and magnesia, treat the filtrate from the precipitate of alumina and ferric oxide as directed in the analysis of limestone.

The best method of determining the sodium and potassium is that of Professor J. Lawrence Smith (*Am. Jour. Sci. and Arts*, Vol. I., 1871, p. 269) for separating the alkalies from silicates. The method is described in his own words: "The silicate is to be well pulverized in an agate mortar; for the analysis I take  $\frac{1}{2}$  gm. or 1 gm.; the former is most commonly used, as being sufficient, and best manipulated in the crucible used; a gramme, however, may be conveniently employed. The weighed mineral is placed in a large agate mortar, or, better, in a glazed porcelain mortar, of  $\frac{1}{2}$  to 1 pint capacity. Weigh out an equal quantity of granular sal-ammoniac (a centigramme more or less is of no consequence), put it in the mortar with the mineral, rub the two together intimately; after which, add 8 parts of carbonate of lime, in three or four portions, and mix intimately after each addition; empty the contents of the mortar completely upon a piece of glazed paper, that ought always to be under the mortar, and introduce into the crucible. The crucible is tapped gently upon the table and the contents settled down.

"It is then clasped by a metallic clamp in an inclined position, or it is placed in the support referred to in the latter part of this article, leaving outside about  $\frac{1}{4}$  or  $\frac{1}{2}$  inch ; a small Bunsen burner is now placed beneath the crucible, and the heat brought to bear just about the top of the mixture, and gradually carried toward the lower part, until the sal-ammoniac is completely decomposed, which takes about 4 or 5 minutes ; heat is then applied in the manner suggested, either with the blast or with the burner referred to, acting by its own draught, and the whole kept up to a bright red heat for about from 40 to 60 minutes. It is well to avoid too intense a heat, as it may vitrify the mass too much. The crucible is now allowed to cool, and when cold, the contents will be found to be more or less agglomerated, in the form of a semi-fused mass. A glass rod, or blunt steel point, will most commonly detach the mass, which is to be dropped into a platinum or porcelain capsule, of about 150 c. c. capacity, and 60 or 80 c. c. of distilled water is added. In the course of a longer or shorter space of time, the mass will slake and crumble after the manner of lime ; still better, this may be hastened by bringing the contents of the capsule to the boiling-point, either over a lamp or water-bath. At the same time, water is put into the crucible, to slake out any small particles that may adhere to it, and, subsequently, this is added to that in the capsule, washing off the cover of the crucible also.

"After the mass is completely slaked, the analysis may be proceeded with, although, as a general thing, I prefer to allow the digestion to continue 6 or 8 hours, which, however, is not necessary. If the contents of the crucible are not easily detached, do not use unnecessary force, as the crucible may be injured by it, but fill the crucible to about two thirds of its capacity with water, bring almost to the boiling-point, and lay it in the capsule, with the upper portion resting on the edge ; the lime will slake in the crucible, and then may be washed thoroughly

into the dish, and, as before, the cover is to be washed off.

"We have now, by this treatment with water, the excess of lime slaked into a hydrate, and some of the lime, combined with the silica and other ingredients of the silicate, in an impalpable form; in solution there is the excess of the chloride of calcium formed in the operation, and all the alkalies originally contained in the mineral as chlorides, and all that now remains to be done is to filter, separate the lime as carbonate, and we have nothing left but the chlorides of the alkalies. To do this I proceed as follows:

"Throw the contents of the capsule on a filter (the size preferred for the quantity above specified is one 3 to 3½ inches in diameter), wash well, to do which requires about 200 c. c. of water; the washing is executed rapidly. The contents of the filter (except in those cases where the amount of the mineral is very small, and there is no more for the estimation of the other constituents) is of no use, unless it be desired to heat again, first adding a little sal-ammoniac to see if any alkali still remains in it, a precaution I find unnecessary. The filtrate contains, in solution, all the alkalies of the mineral, together with some chloride of calcium and caustic lime; to this solution, after it has been placed in a platinum or porcelain capsule, is added a solution of pure carbonate of ammonia (equal to about 1½ gms. is required). This precipitates all the lime as carbonate; it is not, however, filtered immediately, but is evaporated over a water-bath, to about 40 c. c., and to this we add again a little carbonate of ammonia, and a few drops of caustic ammonia, to precipitate a little lime that is re-dissolved by the action of the sal-ammoniac on the carbonate of lime. Filter on a small filter (2 inches), which is readily and thoroughly washed with but a little water, and the filtrate allowed to run into a small beaker glass. In this filtrate are all the alkalies as chlorides, and a little sal-ammoniac; add a drop of a solution of carbon-

ate of ammonia, to make sure that no lime is present. Evaporate over a water-bath in a tared platinum dish, in which the alkalies are to be weighed; the capsule used is about from 30 to 60 c. c. capacity, and during the evaporation is never filled to more than two thirds its capacity. After the filtrate has been evaporated over the water-bath to dryness, the bottom of the dish is dried, and, on a proper support, heated very gently, by a Bunsen flame, to drive off the little sal-ammoniac. It is well to cover the capsule with a piece of thin platinum, to prevent any possible loss by the spitting of the salt after the sal-ammoniac has been driven off. Gradually increasing the heat, the temperature of the dish is brought up to a point a little below redness, the cover being off (the cover can be cleansed from any sal-ammoniac that may have condensed by heating it over the lamp). The capsule is again covered, and when sufficiently cooled, before becoming fully cold, is placed on the balance and weighed. This weight gives, as chlorides, the amount of alkalies contained in the mineral. If chloride of lithium be present, it is necessary to weigh quickly; for this salt, being very deliquescent, attracts moisture rapidly. It not unfrequently occurs that the chlorides, at the end of the analysis, are more or less colored with a small quantity of carbon, arising from certain constituents in carbonate of ammonia; the quantity is usually very minute, and in no way affects the accuracy of the analysis. In selecting pure carbonate of ammonia for analytical purposes, it is well to select specimens that are not colored by the action of light. It only now remains to separate the alkalies by the known methods."

The crucible and burner employed by Professor Smith in separating the alkalies from silicates are of his own devising, and excellent for the purpose. A description and drawing of them will be found in Croke's *Select Methods*, p. 409, in the chapter on decomposition of silicates.

To separate the sodium and potassium and determine



them, dissolve the combined chlorides (after weighing them) in 20 or 30 c. c. of warm water. Should the solution be complete, transfer the solution to a small porcelain dish, add 3 or 4 drops of hydrochloric acid, and as much solution of platinum tetrachloride as contains an amount of the salt equivalent in weight to four times that of the combined chlorides present, and determine the potassium as directed in the analysis of potassium alum. Should the combined chlorides not go completely into water solution, filter, evaporate the filtrate in a platinum dish as before, and proceed as directed above. The solution in water must be complete. Any insoluble residue can not be alkaline chloride, and as the sodium is estimated by difference, it would falsify the results. Deduct the weight of potassium found, calculated to potassium chloride, from the weight of the combined chlorides. The difference will be sodium chloride. Calculate the per cent of  $K_2O$  and  $Na_2O$ .

Ignite 1 gm. of feldspar, and from loss calculate per cent of moisture and organic matter.

Lithium is sometimes found in feldspar. When such is the case, it is to be looked for in the solution of the alkaline chlorides.

Make the solution slightly acid, evaporate to dryness at  $120^{\circ}C.$ , add a mixture of equal parts of absolute alcohol and anhydrous ether, wash into a flask with the same, digest for 24 hours, shaking occasionally, decant on a filter, and treat with smaller quantities of the mixture of alcohol and ether. Finally, wash on the filter, with the same mixture, until the residue gives no evidence of the presence of lithium before the spectroscope. (*Pogg. Anal.*, 66, 79.)

As some sodium and potassium chlorides may be dissolved with the lithium chloride, evaporate off the alcohol and ether at low heat, just to dryness, and treat the impure lithium chloride in the same way. Should any residue of sodium and potassium chloride be left undis-

solved, filter it out, and add it to the first one. To the alcoholic solution add 20 or 30 c. c. of water, and boil out the alcohol and ether, add to the solution a sufficient quantity of pure sodium phosphate, and enough pure sodium hydrate to keep the reaction alkaline, and evaporate the mixture to dryness; pour water over the residue, in sufficient quantity to dissolve the soluble salts with the aid of a gentle heat, add an equal volume of ammonia, digest at a gentle heat, filter after 12 hours, and wash the basic phosphate of lithia with a mixture of equal volumes of water and ammonia. Evaporate the filtrate and washings to dryness, and treat the residue in the same way as before. Should any more lithium phosphate be obtained, add this to the principal quantity. Dry the precipitate, brush it from the filter as perfectly as possible into a clock-glass, burn the filter in a weighed crucible, add the precipitate, and ignite again, at a moderate red heat. Cool and weigh the basic lithium phosphate ( $\text{Li}_3\text{PO}_4$ ).

Dissolve the residue of sodium and potassium chlorides in water, and treat as before for the determination of sodium and potassium, when no lithium is present.

## CHAPTER XI.

### LIMESTONE.

The stone may contain lime, magnesia, iron, alumina, silica, carbonic acid, sulphur, phosphoric acid, water, and organic matter, also manganese, chlorine, fluorine, alkalies, and even other constituents in minute quantities. The lime may exist as carbonate or sulphate, the magnesia as carbonate or silicate, the iron as sulphide (pyrites) or oxide, and the silica as quartz or as silicic acid combined with bases.

The more common constituents, and those required to be determined for technical purposes, are lime, magnesia, alumina, iron, silica, carbonic acid, phosphoric acid, and sulphur.

For an analysis of this character, dry a few gms. of the finely pulverized stone, to constant weight at 150° C., and keep it in a stoppered bottle. Weigh 1 gm. of the dry powder, transfer it to a small beaker, add 20 c. c. of water, cover the beaker with a convex glass, add 5 c. c. of concentrated hydrochloric acid, 1 c. c. of concentrated nitric acid, and heat slowly to boiling. Filter, and wash with 30 or 40 c. c. of hot water, and proceed at once to evaporate the filtrate and washings over a water-bath. Dry the filter and any undissolved residue, ignite them in a small platinum crucible until the carbon of the filter is entirely consumed, add 1 or 2 gms. sodium carbonate, and 0.100 gm. sodium nitrate, and fuse until the contents of the crucible are fluid. Remove the fused mass from the crucible with water, dissolve off any adhering particles with hydrochloric acid, and add the solution to the vessel containing the principal contents of the crucible, keeping it covered to avoid loss by effervescence, also adding more

hydrochloric acid if necessary to render the solution acid. Boil out free carbonic acid, and combine with the principal solution on the water-bath. Evaporate all to dryness, transfer to an air-bath, and heat at a temperature of about 110° C. until the odor of hydrochloric acid disappears. Then add 1 c. c. of concentrated hydrochloric acid, and 20 c. c. of water, heat to incipient boiling, dilute with 50 c. c. of water, filter, and wash with hot water, until the washings show no turbidity when treated with silver nitrate (using only 2 or 3 drops of the wash-water at a time, and not beginning to test until 40 or 50 c. c. of it have passed through the filter). Dry the funnel and contents in an air-bath, at a temperature of about 110° C., ignite in a weighed crucible (observing the precautions given in the analysis of feldspar), cool, and weigh the silica.

To the filtrate from the silica, add ammonia to alkaline reaction, to precipitate the aluminum and ferric hydrates, boil out excess of ammonia, allow the precipitate to settle, decant the clear fluid on a filter, and, as some lime and magnesia may be carried down by the precipitate of hydrates, dissolve it in the beaker, with as little dilute hydrochloric acid as possible, re-precipitate by adding a slight excess of ammonia, and boiling as before. Filter, wash, dry, and weigh the alumina and ferric oxide together. Consult analysis of potassium alum, and that of ammonia-iron-alum.

If it be desired to determine the alumina and ferric oxide separately, proceed as directed in the analysis of feldspar.

Should the filtrate and washings from the hydrates exceed 100 c. c., concentrate to that bulk, if possible, and add 1 c. c. of ammonia. If the ammonia produce a precipitate other than aluminum or ferric hydrate, acidify the solution with hydrochloric acid, boil for a minute, and then make it alkaline again with ammonia. This is done to introduce a sufficient amount of ammonium chloride to prevent the precipitation of magnesium hydrate. Then add 40 c. c. of a solution of ammonium oxalate (pre-

pared by dissolving 1 part of the oxalate in 24 parts of water), enough to precipitate all the lime as oxalate, and convert the magnesia also into oxalate, which remains in solution. Fresenius says this excess is absolutely indispensable to insure complete precipitation of the lime, as calcium oxalate is slightly soluble in magnesium chloride, not mixed with ammonium oxalate. (See his *Experiment* No. 92, p. 600.) After adding the ammonium oxalate, heat just to boiling and allow the fluid to stand undisturbed for some time. After the precipitate has settled perfectly, decant the clear fluid through a filter, wash by decantation once with about 25 c. c. of hot water, and set this filtrate aside as filtrate No. 1. Then dissolve the precipitate of calcium oxalate (mixed with a little magnesium oxalate) in the beaker, with as little hot dilute hydrochloric acid as possible. Should any of the precipitate have passed over on the filter, wash it back into the acid solution, dilute, if necessary, to about 50 c. c. with hot water, make alkaline with ammonia, add 5 or 6 c. c. of ammonium oxalate solution, stir, and allow the precipitate to settle. When it has perfectly subsided, filter through the previous filter, transfer the precipitate to the same, wash it thoroughly with hot water, and determine the lime as directed in the analysis of calcium carbonate.

The first filtrate contains the larger portion of the magnesia, and the second the remainder. (See Fres., *Experiment* No. 93, p. 600.) Acidify the *second* filtrate and washings with hydrochloric acid, concentrate to small bulk, and add it to the first. Do not attempt to concentrate the first filtrate.

To determine the magnesia, make the combined filtrates from the calcium oxalate alkaline with ammonia, if not already so, add 30 c. c. of the ordinary solution of hydrodisodium phosphate, and determine the magnesia as directed in the analysis of magnesium sulphate.

To insure the recovery of all the magnesium, either evaporate the filtrate from the magnesium phosphate to

Ammonium  
oxalate

50

200

dryness, in a platinum dish, burn out the ammonium chloride, dissolve the residue in water containing a few drops of hydrochloric acid, and proceed as in the first instance; or, concentrate to small volume, add 4 or 5 c. c. strong nitric acid, evaporate to dryness, add 4 or 5 c. c. strong hydrochloric acid, evaporate nearly dry, dissolve in water, and determine magnesium as before.

(See J. Lawrence Smith, in *Am. Chem.*, Vol. III., p. 201.)

102  
Determine the carbonic acid by one of the methods given in analysis of calcite; or, if the stone contains no organic matter, fuse 4 gms. vitrified borax in a platinum crucible, cool and weigh, then transfer 1 gm. of pulverized and well-dried stone to the crucible, and weigh again. Then heat gradually to redness, and continue until all is fused; cool and weigh. The loss of weight is carbonic acid. (See Fres., § 139.)

15  
To determine the sulphur, dissolve 5 gms. in a mixture of 15 c. c. of strong hydrochloric acid, 5 c. c. of strong nitric acid, and 10 c. c. of water, in a covered casserole, heat to boiling, and when effervescence ceases, remove the cover, add 10 c. c. strong hydrochloric acid, and evaporate to dryness to expel nitric acid. Then add to the dry mass 1 c. c. of concentrated hydrochloric acid and 50 c. c. of water, and heat just to boiling. Filter out any residue, and wash with about 50 c. c. of hot water. Nearly neutralize the filtrate with ammonia, add 2 c. c. of barium chloride solution (containing 1 part of the salt in 10 parts of water), treat the precipitate of barium sulphate as in the analysis of magnesium sulphate, and calculate the sulphur.

pyr  
To determine the phosphoric acid, dissolve 5 gms. of the stone in 10 c. c. of strong nitric acid, and 30 c. c. of hot water, in a casserole covered with a convex glass. When effervescence ceases, remove the cover, and evaporate to dryness. To the dry mass add 5 c. c. of strong nitric acid, and 50 c. c. of water, and boil. Then filter, wash with about 50 c. c. of water, nearly neutralize with ammonia,

add 25 c. c. of molybdic acid solution, and allow to stand for some hours in a warm place. Should a yellow precipitate appear, filter it out, and wash it with molybdic acid solution (diluted with an equal volume of water). Dissolve the precipitate through the filter into a small beaker with the smallest possible amount of dilute ammonia, add 2 c. c. of magnesium mixture, and proceed as directed in the analysis of hydro-disodium-phosphate. Should a second precipitate appear in the filtrate from the first precipitate of phospho-molybdate, filter it out and treat it in the same way. Calculate the per cent of phosphoric acid, as in analysis of hydro-disodium-phosphate.

It is well after dissolving the precipitate of phospho-molybdate in ammonia, to let the solution stand for some hours, to allow the silica to separate from any silico-molybdate that may possibly be present, before adding the magnesium mixture. Should any silica be deposited, by the decomposition of silico-molybdate in the ammoniacal solution, filter it out, add the magnesium mixture, and proceed as above.

To determine the water, as some may remain after drying the limestone at 150° C., proceed as directed in the analysis of hydro-disodium phosphate, weighing it after absorption in calcium chloride.

To determine the organic matter the same method can be followed as that suggested for the determination of carbonic acid, in anhydrous carbonates, by fusion with borax. (See Fres., § 139—II.—c.) The loss of weight will be carbonic acid, water, and organic matter. The difference between this and the sum of the weights of carbonic acid and water previously determined will be the weight of organic matter. Of course, the fusion with borax must be carefully done, and the determination of carbonic acid and water be accurate, to give correct results.

Another method is, to dissolve 15 or 20 gms. of the limestone in dilute hydrochloric acid, heat it gently to expel carbonic acid, filter out any undissolved residue

through ignited asbestos, wash it well with water, dry it, transfer it, with the asbestos, to a platinum boat, introduce the boat into a combustion-tube of hard glass containing oxide of copper, and ignite it in a current of dry oxygen, absorbing the resulting carbonic acid, and from it calculating the carbon, 58 parts of which, according to Petzholdt, correspond to 100 parts of humus. (See *Jour. f. Prakt. Chem.*, LXIII., 194.)

To determine barium, strontium, and manganese, evaporate to dryness the filtrate from the residue used for the determination of organic matter, and heat in an air-bath at 100° C., until the odor of hydrochloric acid disappears. Then moisten with hydrochloric acid, digest with hot water, filter, and wash. The residue will consist of silica, and perhaps baryta, and strontia in the form of sulphates; while the filtrate will contain the manganese, with other constituents of the limestone.

Expel the silica from the residue with ammonium fluoride and sulphuric acid, in the manner described in the analysis of feldspar. If any residue remain, fuse it with sodium carbonate, digest with hot water, filter, and wash well. Barium and strontium will remain on the filter as carbonates. Dissolve them through the filter with dilute hydrochloric acid, nearly neutralize the solution with ammonia, and add a few drops of sulphuric acid, and allow to stand for some hours. Should a precipitate of barium sulphate, and perhaps strontium sulphate form, filter it out and wash it, and allow the filtrate and washings to run into a small flask. Then stop the point of the funnel, fill the filter with a strong solution of ammonium carbonate, and allow it to stand for 12 hours. By this means, the strontium sulphate will be converted into carbonate, while the barium sulphate will be unattacked. Remove the plug from the point of the funnel, allow the fluid to run into the flask with the first filtrate, wash with hot water, and run dilute hydrochloric acid through the filter into the flask; the object of using



which is to prevent loss by effervescence by the contact of the acid with the solution of alkaline carbonate below. Finally, wash with water, dry the filter and contents, and determine the barium sulphate as usual.

To the combined filtrates in the flask add ammonia and ammonium carbonate, and if a precipitate of strontium carbonate forms, filter it through a very small filter, wash with dilute ammonia, dry, ignite, and weigh the strontium carbonate. Be careful to clean the filter well, and ignite it separately. (See Fres., §§ 72 and 102.)

To the first filtrate from the silica, baryta, and strontia add a few drops of nitric acid, boil, dilute, nearly neutralize with sodium carbonate, add excess of sodium acetate, boil and filter out the ferric hydrate, alumina and phosphoric acid, wash slightly, concentrate to small bulk, filter again if necessary, run the solution, rendered alkaline by a few drops of ammonia, into a small flask, nearly fill the flask, add freshly-prepared ammonium sulphide, cork the flask, and set it aside for 24 hours for the manganese sulphide to precipitate. When the manganese sulphide has entirely settled, decant off the clear fluid into a beaker, not on a filter, wash by decantation into a beaker 3 or 4 times, with water containing ammonium sulphide and a little ammonium chloride, and then on a filter with the same. Then transfer the moist precipitate to a small beaker, add hydrochloric acid, warm until the mixture smells no longer of hydrogen sulphide, dilute slightly, filter, and wash carefully. Then heat the fluid to boiling, remove the heat, add solution of sodium carbonate until the fluid is distinctly alkaline, boil until the carbonic acid is expelled, filter, wash with hot water until the washings are not alkaline to test-paper, dry, ignite, cool, and weigh the manganous-manganic oxide ( $Mn_3O_4$ ), and calculate the manganous oxide ( $MnO$ ).

To determine the chlorine, dissolve 40 or 50 gms. of the limestone in nitric acid, filter, if necessary, and determine the chlorine as directed in the analysis of barium chloride.

To determine the fluorine, dissolve 40 or 50 gms. of the limestone in acetic acid, filter, and in the residue determine the fluorine, by fusing and proceeding as directed in the analysis of calcium fluoride.

To determine the alkalies, dissolve about 20 gms. of the mineral in hydrochloric acid, add chlorine water and heat for a short time. Should there be any residue, filter it out and decompose it by J. Lawrence Smith's method, given in analysis of feldspar. Combine the filtrate, which may contain some alkali, with the main solution. Then add ammonia in slight excess, and ammonium carbonate, and allow the solution to stand for several hours; after this, filter, wash, evaporate the filtrate and washings to dryness, in a platinum dish, and expel the ammonia salts by igniting to a point just below redness. Dissolve in water, add solution of barium hydrate, until the fluid is decidedly alkaline, filter and wash well, and add to the filtrate solution of ammonium carbonate as long as it produces a precipitate, allow the fluid to stand for a short time, filter out the barium carbonate, and wash it until the washings do not render silver nitrate turbid. Then evaporate the filtrate in a weighed platinum dish, after adding a drop of hydrochloric acid, ignite to faint redness, cool, and weigh the mixed chlorides of the alkalies. It is well to dissolve in water, and repeat the treatment with barium hydrate and ammonium carbonate, and again evaporate and weigh. Separate the alkalies, and determine them as directed in analysis of feldspar.

## CHAPTER XII.

### CLAY.

Clay is derived principally from the decomposition of feldspar, or rather feldspathic rocks, and varies in composition and color, on account of varying quantities of feldspar sand (or feldspar reduced to a granular condition and not decomposed), quartz in the form of sand, lime, magnesia, oxide of iron, and manganese. Sometimes oxide of titanium and other minerals in small quantities are found.

The kinds of clay more commonly known are common brick clay, ordinary pottery clay, slate, fire-clay, and kaolin or porcelain clay. The difference between them is due less to the character of the constituents than to their relative quantity.

It is sometimes necessary to make a mechanical analysis by separation of the coarse from the fine parts. For description of methods, and of apparatus, consult *Jour. f. Prakt. Chem.*, XLVII., 241, and *Am. Jour. Sci. & Arts*, 3d series, VI., 288.

For the chemical analysis dry 20 or 30 gms. of the finely-pulverized clay at a temperature of 100° C. to constant weight, and keep the powder in a well-corked bottle.

The loss of weight in drying will be equivalent to the water.

Fuse 1 gm. of the dry powder with a mixture of equal parts by weight of sodium and potassium carbonates, and proceed exactly as directed in the analysis of feldspar, for the determination of silica, oxide of iron, alumina, lime, and magnesia.

After weighing the silica, expel it by Rose's method, with ammonium fluoride, and test any residue which remains qualitatively for titanium. Should any be

detected, fuse 5 gms. of the feldspar with sodium fluoride and acid sodium sulphate, as directed in partial analysis of iron ore, bring into cold water solution, add excess of potassium hydrate, filter out the precipitated titanium dioxide, wash, dry, transfer the precipitate to a capacious platinum crucible, burn the filter and add the ash, and fuse all with 10 or 12 times the weight of acid sodium sulphate. Cool and digest with concentrated sulphuric acid. When the mass is cool, dissolve it in cold water, and precipitate the titanium dioxide by boiling. (Compare analysis of titaniferous iron ore, *Note 7*.)

For the determination of manganese and other constituents, consult analysis of limestone.

Determine the alkalis as in analysis of feldspar.

To ascertain how much of the silica found exists in combination with the bases of the clay, how much as hydrated acid, and how much as quartz sand, or as a silicate present in the form of sand, proceed as follows. (Compare *Fres. Quant. Anal.*, 5th ed. 1865, § 236.)

Let *A* represent silica in combination with bases of the clay.

Let *B* represent hydrated silicic acid.

Let *C* represent quartz sand, and silicates in the form of sand, *e. g.*, feldspar sand.

Dry 2 gms. of the clay at a temperature of 100° C., heat with sulphuric acid, to which a little water has been added, for 8 or 10 hours, evaporate to dryness, cool, add water, filter out the undissolved residue, wash, dry, and weigh ( $A+B+C$ ). Then treat it with sodium carbonate as directed by Rose, p. 923. Transfer it, in small portions at a time, to a boiling solution of sodium carbonate contained in a platinum dish, boil for some time, and filter off each time, still very hot. When all is transferred to the dish, boil repeatedly with strong solution of sodium carbonate, until a few drops of the fluid, finally passing through the filter, remain clear on warming with ammonium chloride. Wash the residue, first with hot water, then (to insure the

removal of every trace of sodium carbonate which may still adhere to it) with water slightly acidified with hydrochloric acid, and finally with water. This will dissolve  $(A+B)$ , and leave a residue  $(C)$  of sand, which dry, ignite, and weigh.

To determine  $(B)$  boil 4 or 5 gms. of the clay (previously dried at  $100^{\circ}\text{C}.$ ) directly with a strong solution of sodium carbonate, in a platinum dish as above, filter and wash thoroughly with hot water. Acidify the filtrate with hydrochloric acid, evaporate to dryness, and determine the silica as usual. It represents  $(B)$  or the hydrated silicic acid.

Add together the weights of  $(B)$  and  $(C)$ , thus found, and subtract the sum from the weight of the first residue  $(A+B+C)$ . The difference will be the weight of  $(A)$  or the silica in combination with bases of the clay.

If the weight of  $(A+B+C)$  found here be the same as that of the silica found by fusion in a similar quantity, in the analysis of the clay, the sand is quartz, but if the weight of  $(A+B+C)$  be greater, then the sand contains silicates.

The weight of the bases combined with silica to silicates can be found by subtracting the weight of total silica found in 1 gm. in the regular analysis, from the weight of  $(A+B+C)$  in 1 gm.

## CHAPTER XIII.

## MANGANESE ORE.

*Mu*

If it is required to determine the amount of metallic manganese that an ore will yield, dissolve 1 gm. of the ore (finely pulverized, and previously dried by exposure in an air-bath, to a temperature of 100° C. for 6 hours), in a mixture of about 10 c. c. of concentrated hydrochloric acid, 2 c. c. of strong nitric acid, and 10 c. c. of water, in a small flask. When the ore is decomposed, filter out the insoluble residue, which should be light colored, and wash well. Pour filtrate and washings into a flask, of a capacity of at least 1 litre, add a saturated solution of crystallized sodium carbonate, little by little, until the fluid becomes dark red in color, but remains clear, thus showing that not quite all the free hydrochloric acid is neutralized. Then add a solution of about 5 gms. of sodium acetate, dilute to 500 c. c., heat to boiling, and continue boiling for 5 minutes. Then remove the heat, allow the precipitate of basic acetates of iron and alumina to settle, filter hot, and wash slightly.

*Sodium  
Acetate  
Solution*

The water required to remove the precipitate from the flask to the filter will be sufficient to wash it. Begin at once to evaporate the first filtrate, and while doing so, dissolve the precipitate in as little hot hydrochloric acid as possible, pour the solution back into the flask, repeat the precipitation in the same way, filter, and wash moderately. Add this filtrate to the first one, and concentrate both to 700 c. c. if possible. It is better to use a capacious porcelain dish for the purpose. To this concentrated solution, add sodium carbonate, until a slight permanent precipitate is formed, and then acetic acid until it is dissolved. Heat to boiling, remove the heat, add bromine water until the

solution has a decided color, and continue to heat to a point just below boiling, until the fluid becomes colorless. Remove the heat, allow the precipitate to settle, add a little more bromine water carefully, so as not to disturb the precipitate, and heat again, as before, until the fluid loses the bromine color. Continue this treatment until the bromine no longer produces a precipitate. Filter out the precipitate of manganese oxide, wash slightly, and, to be sure that the filtrate contains no manganese, neutralize it again with sodium carbonate, acidify it with acetic acid, and proceed as before. When the manganese oxide is all precipitated, transfer, with a spatula, as much of the precipitate as possible from the filters to a small beaker, dissolve what oxide may remain on the filters by pouring hot dilute hydrochloric acid through them into the beaker, and heat to effect solution. Heat the solution to incipient boiling, remove the heat, add solution of sodium carbonate until the fluid is alkaline, and boil until carbonic acid is expelled. Usually, boiling for 5 or 10 minutes will effect this. Then, filter out the manganese carbonate, and wash with hot water until the washings do not turn reddened litmus-paper blue. To test this, hold a narrow strip of the paper against the point of the funnel, so as to bring it in contact with the washings, as they run through. Finally, dry the precipitate, ignite it in a weighed crucible, cool, and weigh the manganoso-manganic oxide ( $Mn_3O_4$ ), and calculate the manganese. After weighing, it is well to ignite the precipitate, and weigh again. If the precipitate is very small, it may be ignited rolled up in the filter.

If the ore contains very little iron oxide, the method of neutralizing the acid solution with sodium carbonate until it becomes dark red, cannot be followed, as there may not be sufficient iron to give the color. In such a case, add solution of sodium carbonate until a very slight permanent precipitate is formed, and then hydrochloric acid, drop by drop, until the solution is slightly acid, and, finally, a solu-

tion of about 5 gms. of sodium acetate, and then proceed as directed above.

If the ore contains silicate of manganese, fuse with sodium carbonate, and then dissolve in acid, and proceed as above.

In all cases where the acid fails to decompose the ore, leaving a dark residue, it is better to decompose the residue by fusion, dissolve the fused mass in acid, and add the solution to the principal one.

If the ore is completely decomposed by acid in the first instance, only a white, pulverulent, siliceous residue should be left.

The commercial value of manganese ore depends chiefly upon the quantity of chlorine it will yield when treated with hydrochloric acid.

By available oxygen is meant the excess of oxygen over the 1 atom combined with manganese to form monoxide, and, as only half of the oxygen of manganese dioxide is available, 16 parts of oxygen are equivalent to 87 parts of manganese dioxide, and, as in the decomposition of 1 molecule of manganese dioxide by hydrochloric acid 2 atoms of chlorine are liberated, 16 parts of oxygen are also equivalent to 71 parts of chlorine.

To determine the available oxygen, introduce into flask "B" of the apparatus described in the analysis of calcite, about 3 gms. of the ore, very finely pulverized, and carefully dried at 100° C. The best method of determining the quantity of ore taken is that described in the analysis of potash alum, by weighing a tube containing pulverized and dried ore, shaking out the desired quantity, again weighing the tube and determining the weight of ore taken by the loss. Introduce also into the flask about 7 or 8 gms. of neutral potassium oxalate, and as much water as will fill it to about one quarter. Fill flasks "A" and "C" of the apparatus about one quarter full of pure concentrated sulphuric acid. Put the apparatus together, weigh it, and proceed as directed in the analysis of cal-



cium carbonate, for the determination of carbonic acid by loss, drawing about 1 litre of air through the flasks, very slowly, by means of an aspirator, not allowing air-bubbles to pass faster than 2 per second. The heat generated by the union of the water and sulphuric acid is sufficient. The difference in the weight of the apparatus, before and after the operation, is equivalent to the weight of carbonic acid lost. (Fres., § 230.)

The method of calculating the available oxygen is evident upon an examination of the equation representing the reaction :



Two molecules of carbonic acid are equivalent to one molecule of manganese dioxide, *i. e.*, 88 parts by weight of carbonic acid represent 87 parts by weight of manganese dioxide. Therefore, if the weight of carbonic acid is multiplied by 87, and the product divided by 88, the quotient will be the weight of manganese dioxide. As only one half of the oxygen of manganese dioxide is available, it is calculated by a simple proportion, *viz.*, 87 : 16 = weight of  $\text{MnO}_2$  ; weight of available O.

Some ores of manganese contain carbonates, the carbonic acid of which must, of course, be removed before the analysis is made. If such be the case, introduce the ore as before into flask "B," fill it about one quarter full with water, add dilute sulphuric acid (1 part acid to 5 parts water), little by little, until effervescence ceases, and the fluid remains acid after boiling out the carbonic acid. Then neutralize the excess of acid with sodium or potassium hydrate, free from carbonic acid, add the usual quantity of neutral oxalate, and proceed as before. (*Zeitschrift f. Analyt. Chem.*, 1, 48.)

Another method is that known as the iron method. Fresenius's directions (p. 512) are to dissolve in a long-necked flask, placed in a slanting position, 1 gm. of piano-forte wire, and dissolve it in pure concentrated hydrochloric acid; then weigh about 0.600 gm. of the ore, in a little

tube, drop this with its contents into the flask, and heat cautiously until the ore is dissolved. One eq. of manganese dioxide, or 87 parts, converts 2 eqs. of iron, or 112 parts, from the state of ferrous to that of ferric chloride. When complete solution has taken place, dilute the contents of the flask with water, allow to cool, rinse into a beaker, and determine the iron still remaining in the state of ferrous chloride with potassium bichromate. (See analysis of ammonio ferric sulphate.) Deduct this from the weight of the wire employed in the process. The difference expresses the quantity of iron, which has been converted by the oxygen of the manganese from ferrous to ferric chloride. This difference, multiplied by 87, and divided by 112, gives the amount of manganese dioxide in the ore.

Pattinson has suggested a modification of this method, in a paper read before the Newcastle-upon-Tyne Chem. Soc., Jan. 27, 1870. His test analyses are very satisfactory. He directs to dissolve about 2 gms. of clean iron wire in a flask holding about 500 c. c., with about 90 c. c. of dilute sulphuric acid, made by adding 3 parts of water to 1 part of the acid. A cork, through which passes a tube bent twice at right angles, is inserted in the neck of the flask, and the flask is heated over a gas flame until the iron is dissolved. The bent tube is placed so as to dip into a small flask or beaker containing a little water. When the iron is quite dissolved, 2 gms. of the finely pounded and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame, until it is seen that the whole of the black part of the sample is dissolved. The water in the small flask or beaker is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well rinsed, and the contents of the flask made up to about 250. or 300 c. c. with distilled water. The amount of iron remaining un-

oxidized in the solution is then ascertained by means of a standard solution of potassium bichromate. The amount the bichromate indicates, deducted from the total amount of iron used, gives the amount of iron which has been oxidized to the ferric form by the manganese ore, and from which can be calculated the percentage of peroxide of manganese contained in the ore. Thus, supposing that 0.250 gm. of iron remained unoxidized, then if 2 gms. of iron were taken at first, 1.750 gms. of iron will have been oxidized by the ore. Then as

$$112 : 87 = 1.750 : 1.359 \text{ gm. MnO}_2$$

which, if 2 gms. of ore were taken for the test, would represent 67.95 per cent of  $\text{MnO}_2$  in the ore.

Standardized solution of potassium permanganate can be used instead of bichromate.

It is frequently of importance to know the amount of hydrochloric acid necessary to decompose an ore of manganese. This can be determined with sufficient accuracy for commercial purposes, by what is called Kiefer's solution. (*Ann. d. Chem. u. Pharm.*, XCIII., 386.)

To prepare the solution, dissolve 15 gms. recrystallized copper sulphate in 100 c. c. of warm water, and add ammonia, with stirring, until the basic salt is *nearly dissolved*. Should the point be overstepped, add more copper sulphate, and repeat. Filter the solution, and add the filtrate from a burette, with constant stirring, to 10 c. c. of half-normal sulphuric acid, until a permanent turbidity is produced, and note the number of c. c. used. As 10 c. c. of half-normal sulphuric acid is equivalent to 0.365 gm. of hydrochloric acid, this, divided by the number of c. c. of the copper sulphate solution used, shows the quantity of hydrochloric acid represented by 1 c. c. of it. This is standard copper sulphate solution.

The next step is to prepare a solution of hydrochloric acid of 1.1 sp. gr., and to 10 c. c. of it add the standard copper sulphate solution, drop by drop, with constant stirring, until the fluid becomes slightly turbid. The

*Kiefer's  
Solution  
or  
Copper  
Sulphate  
Soln.  
H. of Manganese  
Sulphate*

number of c. c. of copper sulphate solution used multiplied by the previously ascertained value of 1 c. c. of it, gives the quantity of hydrochloric acid in the hydrochloric acid solution of 1.1 sp. gr.

Then, into a flask, through the cork of which passes a tube about 3 feet long, and of about one quarter of an inch diameter, and bent slightly from the perpendicular, introduce 1 gm. of the manganese ore to be tested and 10 c. c. of the standardized hydrochloric acid, and heat gently until the ore is decomposed, and then more strongly for a few minutes until the chlorine is expelled.

The object of the long tube is to condense the vapor, and allow the fluid to run back into the flask. To insure this, it is well to wrap it with a wet cloth and keep it cool.

After the chlorine is expelled, cool the flask, add 25 c. c. of cold water, filter, and wash with 25 or 30 c. c. of cold water. Then to the filtrate add, as before, standard copper sulphate solution, until the fluid is slightly turbid. The number of c. c. used shows the quantity of free hydrochloric acid present.

The difference between the quantity of hydrochloric acid found in 10 c. c. of the solution of 1.1 sp. gr. before adding it to the ore, and the quantity in 10 c. c. after using it for dissolving the ore, gives the quantity required to dissolve 1 gm. of the ore.

The calculation of the manganese oxides in an ore is best illustrated by an example:

Suppose total Mn = 25.24 per cent and available O = 6 per cent.

Calculate first the available oxygen to make  $\text{MnO}_2$

$$(\text{O}) 16 : (\text{MnO}_2) 87 = 6 : 34.62.$$

Calculate the Mn corresponding to this:

$$(\text{MnO}_2) 87 : (\text{Mn}) 55 = 34.62 : 20.62.$$

Total Mn as above.....	25.24
------------------------	-------

Mn as $\text{MnO}_2$ calculated above.....	20.62
--	-------

Difference.....	4.62 per cent Mn
-----------------	------------------

Calculate this as  $\text{MnO}$ . It is equivalent to 5.96 per cent, since

$$(\text{Mn}) 55 : (\text{MnO}) 71 = 4.62 : 5.96.$$

Calculate  $\text{MnO}_2$  required to combine with this to form  $\text{Mn}_2\text{O}_3$  :

( $\text{MnO}$ ) 71 : ( $\text{MnO}_2$ ) 87 = 5.96 : 7.30.  $\text{MnO} + \text{MnO}_2 = \text{Mn}_2\text{O}_3$ .

$\text{Mn}_2\text{O}_3$ , then, is ( $\text{MnO} = 5.96$ ) + ( $\text{MnO}_2 = 7.30$ ) = 13.26 per cent  $\text{Mn}_2\text{O}_3$ .

Total  $\text{MnO}_2$  calculated from available O = 32.63

Deduct  $\text{MnO}_2$  combining to form  $\text{Mn}_2\text{O}_3 = 7.30$

Difference =  $\text{MnO}_2$  existing as such..... 25.33

Or the ore contains

$\text{Mn}_2\text{O}_3$ ..... 13.23 per cent.

$\text{MnO}_2$ ..... 25.33 per cent.

78

*Sample 1 - 1/2 lb. Pure anhydrous FeO - 1 lb. Fe*  
*1 lb. FeO*

# CHAPTER XIV.

## PARTIAL ANALYSIS OF IRON ORE.

### FOR SILICA, IRON, SULPHUR, AND PHOSPHORUS.

Pulverize 7 or 8 gms. of the ore to impalpable powder in an agate mortar, weigh exactly 5 gms. of the powder, and mix it carefully, in a large clock-glass, with 25 gms. of dry sodium carbonate and 2.5 gms. of sodium nitrate, previously pulverized. Introduce about one third of the mixture into a capacious platinum crucible, provided with a cover, and heat over a strong Bunsen burner until the mass ceases to swell in the crucible from the action of the gases. Then allow the crucible to cool to a point below redness, introduce about the same quantity, and treat it in the same way. Finally, transfer the remainder to the crucible, and, after heating over the Bunsen flame until the contents of the crucible become quiet, apply the strongest heat of a good blast-lamp until the contents are reduced to quiet fusion, or, as will sometimes be the case, a semi-fused mass results, upon which heat seems to have no more effect. Follow the directions given in the analysis of feldspar, for removing the mass from the crucible, and cleansing the latter from adhering particles. When that portion of the contents of the crucible, which is insoluble in water, has entirely settled, pour off the clear fluid into another vessel, add to the residue 20 or 30 c. c. pure concentrated hydrochloric acid, together with the washings of the crucible, and cover, and evaporate on a water-bath nearly to dryness. Then dilute with a little water; and should all be now in solution (except some separated silica), transfer all to the alkaline water solution, cautiously (keeping the vessel covered to prevent loss by effervescence), make the fluid acid with hydrochloric acid, if not already so, heat to boiling to expel car-

bonic acid, transfer to a casserole, evaporate on a water-bath, and heat in an air-bath. (Compare analysis of feldspar.) Should there be any undecomposed ore after the treatment with acid, as directed above, it may be digested once more, with concentrated hydrochloric acid, and the solution added to the first. But if any ore resists this treatment, filter it out, add the filtrate to the other solutions, dry the residue, burn it in a platinum crucible, fuse as before, proportioning the flux to the quantity of residue, and, after bringing all into solution, proceed as before. Should the ore resist this treatment, which is an extreme case, dry and fuse the filtered residue in the way directed by Hart in *Chem. Gaz.*, 1855, 458: "Fuse 8 parts of borax in a platinum crucible, add to the mass in fusion 1 part of finely pulverized ore, stir constantly, and keep the crucible half an hour longer at a bright-red heat, add dry carbonate of soda as long as it causes effervescence, then gradually, and with frequent stirring with a platinum wire, 3 parts of a mixture of equal parts of nitrate of potassa and carbonate of soda, and keep the mass a few minutes longer in fusion. Remove the mass from the crucible with water, dissolve in hydrochloric acid, and combine with the other solutions; evaporate all to dryness on a water-bath, dry in an air-bath, and proceed to the determination of the silica as directed in the analysis of feldspar.

Dilute the acid filtrate from the silica to 500 c. c., and divide it into 3 portions, the first containing 100 c. c., in which the iron and sulphur are to be determined, and the other two containing 200 c. c. each, in which the phosphorus is to be determined in duplicate.

In the first portion, which is equivalent to 1 gm. of the ore, precipitate the ferric hydrate, with an excess of ammonia, filter, wash until a few drops of the wash-water, acidulated with hydrochloric acid, give no reaction with barium chloride solution, for sulphuric acid. Dissolve the precipitate in hot, dilute sulphuric acid, divide

the solution into 2 equal portions, reduce them with amalgamated zinc and platinum in proper bottles, and determine the iron volumetrically with potassium permanganate, as directed in the analysis of ammonio-ferric sulphate. If the ore contain titanous acid, it must be removed before reducing the ferric to ferrous oxide, as the titanium dioxide is also reduced to sesquioxide by the action of the zinc and platinum, and reoxidized by potassium permanganate. Consequently, more permanganate will be decomposed than is required to raise the ferrous to ferric oxide.

For the method of proceeding in such a case, consult analysis of titaniferous iron ore (Note 7).

After precipitating the ferric hydrate from the portion containing 100 c. c., determine the sulphur in the filtrate as directed in the analysis of magnesium sulphate. <sup>p 17</sup>

The phosphorus is to be determined in each of the 2 portions of 200 c. c. by either of the following methods:

First Method.—The ferric oxide, carrying the phosphoric acid, is precipitated from the solution by ammonia, filtered out, and washed moderately (the water required to remove the precipitate to the filter being sufficient). The walls of the glass, in which the precipitation is effected, are washed down by about 25 c. c. of hot concentrated nitric acid. To this the precipitate is transferred by means of a spatula, with occasional stirring. After removing from the filter all of the precipitate that can be conveniently reached by the spatula, the solution is heated, and poured through the filter, and the filter well washed with water into a beaker of medium size. By this means complete solution is effected in a very short time. This solution is now boiled down to very small bulk, to remove all chlorine and excess of nitric acid, diluted to a volume of about 100 c. c., and neutralized by ammonia to a light mahogany color. To this a sufficient quantity of solution of "ammonium molybdate" is added, and the whole kept at a temperature just below

Precipitate  
with  $\text{NH}_4\text{O}^3$

P<sub>2</sub>O<sub>5</sub>



boiling for 2 or 3 hours, and then allowed to stand in a warm place for 12 hours longer. In most cases, 25 c. c. of a solution so prepared that 1 c. c. is equivalent to 0.001 gm. of phosphoric acid will be sufficient. When the precipitate has settled, it is filtered out and washed with ammonium molybdate solution which has been diluted with an equal volume of water. The filtrate is again partially neutralized with ammonia, warmed, and allowed to stand in a warm place for 5 or 6 hours. If any precipitate occurs, it is filtered out, and treated as before, and the filtrate tested again. In rare cases, a third small precipitate forms.

*Molybdate  
Solution*

The washed precipitates of phospho-molybdate are dissolved through the filters with dilute ammonia into the same beaker, and the filters washed with water. As a small amount of ferric oxide, enough to color the filter around the edge, if not more, almost invariably remains after washing, nitric acid is now poured on the filter, drop by drop, allowed to run into the beaker containing the ammoniacal solution, the filter washed with a little water, 4 or 5 c. c. of ammonium molybdate solution added, to separate any phosphoric acid that may be held by the ferric oxide, and enough more nitric acid to render the solution decidedly acid, avoiding however a large excess. By this means, the phospho-molybdate is precipitated free from iron, which may have been carried down with it previously. The acid solution is allowed to stand for a few hours in a warm place, until the supernatant fluid is clear. It is well, although rarely necessary, to test this fluid (after filtering), for another precipitate, by gently warming it, and allowing it to stand for a time. The re-precipitated phospho-molybdate is filtered out, washed with dilute ammonium-molybdate solution, and dissolved with ammonia. To the solution is added enough hydrochloric acid to make it acid, about 0.050 gm. of tartaric acid, then enough ammonia to render it decidedly alkaline, and finally 5 c. c. of "magnesia mixture." The object aimed

at in adding the hydrochloric acid and ammonia is the introduction of a sufficient amount of ammonium chloride, to prevent the precipitation of any magnesium salts from the magnesia mixture; while the tartaric acid is introduced to hold up any trace of iron that may be in the solution.

After adding the magnesia mixture, the whole is set aside in the cold, until the precipitate of ammonio-magnesium-phosphate is entirely formed, when it is filtered, washed with dilute ammonia, dried, ignited, and weighed. Consult analysis of hydro-disodium-phosphate. (Also see article by F. A. Cairns, in *Am. Chem.*, Dec., 1876.)

Second Method.—Heat the hydrochloric acid solution to boiling, remove the heat, and add a saturated solution of pure sodium sulphite (little by little), and more hydrochloric acid, if necessary, until the fluid becomes colorless, showing that the ferric is reduced to ferrous chloride. Then add a little more hydrochloric acid, and boil until the odor of sulphurous acid disappears, keeping up the volume of fluid by occasional addition of hot water. When the odor of sulphurous acid can no longer be detected, if the solution should not have acquired a yellow tint, add enough potassium permanganate solution to oxidize about 0.150 gm. of the ferrous to ferric chloride, then saturated solution of sodium carbonate, until a permanent precipitate is formed, and the solution slightly alkaline. Then make the solution acid with acetic acid, dilute to about 200 c. c., heat to boiling, and continue to boil for 8 or 10 minutes; after which remove the heat and allow the basic acetate of iron to settle completely. It will carry all but perhaps a slight trace of phosphoric acid with it. Filter, and proceed to boil the filtrate for a second small precipitate, to insure the recovery of all the phosphoric acid.

Dissolve the first precipitate by pouring hot hydrochloric acid through the filter. Should it fail to dissolve

all the precipitate, throw the filter into the acid, and digest over heat until the solution is complete. To the clear solution, after filtering, if necessary, add ammonia in excess (without heating), filter out the ferric hydrate, and dissolve it by pouring hot nitric acid through the filter. The reason for dissolving in hydrochloric acid first, is that the basic acetate is apt to contain a quantity of a modification of ferric oxide, very insoluble in nitric acid, but which yields readily to hydrochloric, while the ferric oxide re-precipitated from hydrochloric acid solution by an excess of ammonia is readily soluble in hot nitric acid.

Boil down the nitric acid solution nearly to dryness, in order to expel all chlorine, dilute with hot water to about 100 c. c., nearly neutralize with ammonia, add 25 c. c. ammonium molybdate solution, heat to a point just below boiling for 2 or 3 hours, and allow to stand in a warm place for 12 hours more. After the precipitate has completely subsided, filter and wash with solution of ammonium molybdate, diluted with an equal volume of water. Reserve the filtrate, which may contain a little phosphoric acid, to be used to dilute the nitric acid solution of the second precipitate of basic acetate.

Dissolve the precipitate of phospho-molybdate of ammonium through the filter with dilute ammonia, wash the filter with 20 or 30 c. c. of water, run through the filter, into the ammoniacal solution, enough dilute nitric acid to dissolve any adhering oxide of iron, and render the solution slightly acid, adding at the same time 4 or 5 c. c. of ammonium molybdate solution, and allow all to stand until the precipitate brought out by the nitric acid has entirely settled.

This re-precipitation by means of nitric acid is made to separate any traces of ferric oxide, which will remain in solution in the nitric acid, while the phospho-molybdate precipitates, and can, by filtering and washing with dilute ammonium molybdate solution, be (usually) entirely

freed from iron. Set this precipitate, which contains nearly all the phosphoric acid, on one side, after filtering and washing it with dilute ammonium molybdate until the treatment of the second precipitate of basic acetate is completed.

Bring this second precipitate of acetate into nitric acid solution, in the same way as the first one, boil it down nearly to dryness, dilute with 30 or 40 c. c. of water, nearly neutralize with ammonia, and add to it the filtrate from the first precipitate of phospho-molybdate, reserved for the purpose, together with the filtrate from the re-precipitation of the same by nitric acid. By this means, all phosphoric acid which may not have been precipitated will be in the solution. Should another precipitate appear in this solution, after heating it, and allowing it to stand as before, treat it in the same manner as the first one. Dissolve both precipitates through the filters, which should be of the smallest size, into the same beaker, with as little dilute ammonia as possible, and wash them with 15 or 20 c. c. of water.

Finally acidulate with hydrochloric acid, add about 0.050 gm. of tartaric acid, make alkaline with ammonia, add 5 c. c. magnesia mixture, and allow to stand for 12 hours, and proceed as in analysis of hydro-disodium phosphate. (Compare Fres., *Quant. Anal.*, § 135, p. 275.)

*Appendix 1.* When only the amount of iron in an ore is to be determined, thoroughly mix 1 gm. of the ore with 3 gms. of sodium fluoride, transfer to a large platinum crucible, cover with 12 gms. of coarsely powdered acid sodium sulphate, and fuse for 20 or 30 minutes. Then cool, add concentrated sulphuric acid, fuse to a homogeneous paste, dissolve in water, reduce with zinc and platinum, and titrate with potassium permanganate. As stated before, titanium, if present, must first be removed. (See *Am. Jour. Sci.*, XLV., 178. Clarke.)

*Appendix 2.* If titanium alone is to be determined, fuse the ore in the same way with sodium fluoride and acid

sodium sulphate, treat with sulphuric acid, bring into solution, precipitate the ferric oxide and titanium dioxide, and proceed to determine the latter, as directed in Note 7 of analysis of titaniferous iron ore.

NOTE.—Instead of using sodium carbonate alone to effect the disintegration of the ore, a mixture of sodium carbonate with potassium carbonate (both dry) may be used. The relative proportions should approximate to the ratios of the respective molecular weights), i. e., 106 parts  $\text{Na}_2\text{CO}_3$  to 138.3 parts  $\text{K}_2\text{CO}_3$  (11 to 14 would be sufficiently close).

If the ore is very refractory, the flux proposed by Prof. Dittmar (Phil. Soc. of Glasgow) (*Iron*, Jan., 1876, p. 181, or *Dingl., Polyt. Journ.*, CCXXI., 450) may be used. This is made by fusing together 3 parts of the above mixture of carbonates and 2 parts of borax glass, over a good Bunsen burner, until the carbon dioxide has been driven off. Pour the melt out upon a clean, cold surface, and when cool pulverize it for use; keep in a tightly corked bottle. Use 5 to 6 parts of this flux to one of the ore, and fuse for an hour or two over a burner, stirring from time to time with a stout platinum wire. A small amount of alkaline nitrate may be added to oxidize sulphides, etc. A very high heat, such as might be attained with a blast lamp, is to be avoided, since that would cause the borax to attack the platinum of the crucible.

Any flux which may be used should be carefully tested for the presence of sulphates, when sulphur is to be determined in the ore. If a flux free from sulphate cannot be obtained, the amount present must be determined and a deduction made accordingly.

## CHAPTER XV.

### COMPLETE ANALYSIS OF IRON ORE.

Fuse 5 gms. *Note 1.*

# <i>Solution (a).</i> $\text{Cr}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, \text{TiO}_2, \text{MnO},$ $\text{CaO}, \text{MgO}, \text{etc.}$	<i>Residue (a).</i> $\text{SiO}_2, \text{TiO}_2,$ and perhaps $\text{Fe}_2\text{O}_3$ . <i>Note 2.</i>
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Add  $\text{Na}_2\text{CO}_3$  and Br. *Note 3.*

<i>Precipitate (b).</i> $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, \text{MnO}_2, \text{TiO}_2, \text{CaO},$ $\text{MgO}, \text{etc.}$	<i>Filtrate (b).</i> $\text{CrO}_3$ . <i>Note 4.</i>
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Dissolve in HCl and pass  $\text{H}_2\text{S}$ . *Note 5.*

<i>Filtrate (c).</i> $\text{FeO}, \text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, \text{TiO}_2, \text{MnO}, \text{CaO}, \text{MgO},$ $\text{etc.}$	<i>Precipitate (c).</i> $\text{PtS}_2$ , etc. <i>Note 5.</i>
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Divide into 2 portions. *Note 6.*

$\frac{1}{2}$ of <i>Filtrate (c).</i> $\text{FeO}, \text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, \text{TiO}_2, \text{MnO}, \text{CaO}, \text{MgO},$ $\text{etc.}$	$\frac{1}{2}$ of <i>Filtrate (c).</i> $\text{TiO}_2, \text{FeO}$ . <i>Note 7.</i>
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Oxidize and precipitate acetates. *Note 8.*

<i>Precipitate (d).</i> $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, \text{TiO}_2$ . Dissolve in $\text{HNO}_3$ , dilute and divide. <i>Note 9.</i>	<i>Filtrate (d).</i> $\text{MnO}, \text{CaO}, \text{MgO}, \text{etc.}$ Concentrate and add Br. <i>Note 12.</i>
$\frac{1}{4}$ of <i>Solution of</i> <i>Precip. (d)</i> $\text{P}_2\text{O}_5$ . <i>Note 10.</i>	$\frac{1}{4}$ of <i>Solution of</i> <i>Precip. (d)</i> $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{TiO}_2,$ $\text{P}_2\text{O}_5$ . Add $\text{NH}_4$ $\text{HO}$ . <i>Note 11.</i>
	<i>Filtrate (f).</i> <i>Precipitate (f).</i> $\text{CaO}, \text{MgO}$ . <i>Note 13.</i> $\text{MnO}_2$ . <i>Note 12.</i> 18.
	<i>Precipitate (g).</i> <i>Filtrate (g).</i> $\text{CaO}$ . <i>Note 13.</i> $\text{MgO}$ . <i>Note 14.</i>

S. in separate portion. *Note 15.*

Co, Ni, Zn. *Note 16.*

As in separate portion. *Note 17.*

Alkalies in separate portion. *Note 18.*

Copper. *Note 19.*

Water. *Note 20.*

Chlorine, fluorine, carbonic acid, organic matter. *Note 21.*

Appendix.

Iron ores, besides the ordinary constituents, such as

iron, alumina, manganese, lime, magnesia, sulphur, phosphorus, silica, and water, frequently contain titanium, zinc, carbonic acid, potassium, and sodium, and occasionally chromium, copper, nickel, cobalt, arsenic, and organic matter, and in some rare cases vanadium, tungsten, chlorine, and fluorine, besides other substances in very minute quantities.

*Note 1.*—Fuse 5 gms. of the ore, pulverized to impalpable powder (well mixed with 25 gms. of anhydrous sodium carbonate and 5 gms. of sodium nitrate), in a capacious platinum crucible. Remove the fused mass from the crucible with as little water as possible, allow the solid matter to settle, decant off the clear fluid into another vessel, digest the solid matter with 25 or 30 c. c. of strong hydrochloric acid on a water-bath for an hour or two, renewing the acid, if necessary, and keeping the vessel covered. When all is dissolved, except perhaps some silica and titanium oxide, and no undecomposed ore, add the residue, together with the clear fluid, to the first water solution, and after acidifying with hydrochloric acid, evaporate to dryness as usual, for the determination of silica. Should there be any undecomposed ore, filter it out, wash with water, and dry it. Add the filtrate to the first water solution. Then burn the filter and residue in a capacious platinum crucible, add 6 or 8 gms. of acid potassium sulphate, and fuse for 15 minutes at a temperature scarcely above the fusing point of the latter, then raise the heat somewhat, so that the bottom of the crucible may just appear red, and keep it so for 15 or 20 minutes. The fusing mass should not rise higher than half-way up the crucible. The mass begins to fuse quietly, and abundant fumes of sulphuric acid escape. At the expiration of 20 minutes the heat is increased as much as is necessary to drive out the second equivalent of sulphuric acid, and even to decompose partially the sulphate of iron and chromium. To the fused mass now add 4 or 5 gms. of pure carbonate of soda, heat to fusion, and add

in small portions from time to time during an hour, 3 or 4 gms. of sodium nitrate, maintaining a gentle red heat all the while, then heat for 15 minutes to bright redness, cool, and treat the fused mass with hot water; remove it from the crucible, allow the solid matter to settle, add the clear fluid to the previous solution, digest the residue with strong hydrochloric acid, as directed above, and if the ore is entirely decomposed, add everything to the other fluid. Should there still be undecomposed ore, repeat the treatment.

(See Fres., *Quant. Anal.*, § 223, p. 524.)

After entirely decomposing the ore and combining all the solutions, evaporate them to dryness, first on a water-bath, and then in an air-bath, as usual in the determination of silica. When the mass is thoroughly dry, add 10 c. c. of strong hydrochloric acid, 30 c. c. of water, and heat on a water-bath until everything is dissolved except silica and titanium oxide. Then dilute with 50 or 60 c. c. of water, filter, and wash with about 100 c. c. of 5 per cent hydrochloric acid,

There will be a *residue (a)* of silica and titanic oxide, and a *solution (a)* of the remaining constituents of the ore. Dry *residue (a)*, and reserve *solution (a)*, to be combined with the solution resulting from the re-fusion of the silica, which always contains a portion of the titanic oxide, and usually some ferric oxide, particularly if the quantity of titanic oxide in the ore be large.

Silica

*Note 2.*—Fuse *residue (a)*, containing silica and titanic oxide, and perhaps a little ferric oxide, with 10 or 12 times its weight of acid sodium sulphate, soften the mass by heating it in the crucible with concentrated sulphuric acid, cool thoroughly, and dissolve in about 400 c. c. cold water. Filter out silica, wash with about 100 c. c. of cold water, containing 5 per cent of hydrochloric acid, and add filtrate and washings to *solution (a)*. Dry, ignite, and weigh the residue, which may still contain some titanic oxide. Then treat with concentrated sulphuric acid and



ammonium fluoride, adding a quantity of the latter equal in weight to about 8 times that of the silica. After evaporating off the sulphuric acid and igniting gently, cool and weigh. Then repeat the treatment until the crucible ceases to lose weight. (Compare Rose's directions, in his chapter on silicon, p. 874.) The weight of the silica is estimated from the loss.

Should there be any residue left after the treatment with ammonium fluoride, fuse it with acid sodium sulphate, in the manner directed above, bring it into cold-water solution, and add it to *solution (a)*, which will then contain all the constituents of the ore except silica.

*Note 3.*—To *solution (a)* add sodium carbonate, until it is strongly alkaline, and then, without filtering out the precipitate, bromine water, until it is deeply colored, stirring constantly. After this, add 5 or 6 c. c. of pure bromine, and heat for an hour, with frequent stirring, keeping it alkaline and gradually increasing the heat until the solution boils, and continue to boil gently for another hour. The chromic oxide will be oxidized to chromic acid. Then filter and wash thoroughly with hot water, first by decantation 3 or 4 times, boiling each time with a small amount of water, and then on the filter, until the wash-water runs through colorless. If there be a large amount of chromium in the ore, in order to insure complete separation of it, wash the mass on the filter back into a beaker, with about 200 c. c. of water, and treat again with bromine water and 2 or 3 c. c. of pure bromine, and proceed as before, filtering through the same filter. This will insure complete separation of the chromium from all but traces of the other constituents of the ore, with the exception of manganese, which will also be found in the filtrate as sodium manganate.

There will be a *filtrate (b)*, containing all the chromium as alkaline chromate, and a *precipitate (b)*, containing the principal part of the other constituents of the ore.

*Note 4.*—To *filtrate (b)*, containing chromium, man-

ganese, and traces of other constituents of the ore, add nitric acid to partly neutralize, then 3 or 4 gms. ammonium nitrate, and evaporate until no odor of ammonia is perceptible. Then dilute with 100 c. c. of water, filter, and wash the residue of manganese sesquioxide, silica, alumina, and titanitic oxide, dissolve it in hydrochloric acid, after removing it from the filter, with a little water, dry and burn the filter, and add the ash, together with the solution of the residue, to the solution of *precipitate* (b), or the principal solution of the ore. Into the filtrate, containing only alkaline chromate, after acidifying it with hydrochloric acid, conduct sulphuretted hydrogen to saturation to reduce the chromic acid to sesquioxide. Allow the sulphur to settle entirely, filter, wash, and in the filtrate precipitate the chromic oxide with ammonia. (See Fres., *Quant. Anal.*, § 106, p. 176.) Evaporate the filtrate from the chromium to dryness, ignite the residue, together with the precipitate (if any) produced by sulphuretted hydrogen, dissolve any residue that may be left in hydrochloric acid, and add the solution to that of *precipitate* (b) or the principal solution of the ore.

*Note 5.*—Dissolve *precipitate* (b) in hydrochloric acid, dilute with cold water, and saturate with sulphuretted hydrogen, filter, and wash with cold water. Do not heat, as otherwise titanitic oxide may be precipitated.

There will be a *filtrate* (c) and a *precipitate* (c), which latter may contain platinic sulphide (due to platinum taken from the crucible by the fluxes), and also sulphides of metals of the higher groups, which, if present in sufficient quantity, are to be determined by methods, which will be explained later.

*Note 6.*—Dilute *filtrate* (c) to 500 c. c., if it does not already exceed that volume, and divide it into 2 portions, one containing 100 c. c., or one fifth, and equivalent to 1 gm. of ore, for the estimation of iron and titanium, and another containing 400 c. c., or four fifths, and equivalent to 4 gms. of ore, for the estimation of other constituents.

Should the solution exceed 500 c. c. and be less than 1,000 c. c., dilute to the latter volume, and divide in the same proportion. It is not well to concentrate the solution, by the aid of heat, as some of the titanic oxide may be precipitated, which will necessitate troublesome steps to bring it back into solution.

*Note 7.*—To *one fifth of filtrate (c)*, representing 1 gm. of the ore, add a little potassium chlorate and hydrochloric acid, and boil, in order to oxidize sulphur, and convert the ferrous into ferric oxide. Then precipitate the ferric and titanic oxides by adding pure potassium hydrate in excess, filter, and wash with hot water. By this means all but traces of the alumina will be held in solution, and thus separated from the iron and titanium, with the latter of which it otherwise might afterward be precipitated by boiling. Dissolve the precipitate in dilute sulphuric acid, and increase the volume, by addition of cold water, to about 500 c. c. Then add ammonia, drop by drop, until a permanent precipitate is formed, and sulphuric acid, cautiously, until it is dissolved, and the solution made slightly acid. After this, pass sulphuretted hydrogen until the solution is colorless, thus reducing the ferric to ferrous oxide. Boil for an hour or two, keeping up the volume, by the occasional addition of water containing sulphuretted hydrogen; allow the precipitate to settle, filter, and wash with hot water. Dry the precipitate, and as some iron may, and probably will, have been precipitated with the titanium, fuse with 10 or 12 times its weight of acid sodium sulphate, digest with concentrated sulphuric acid, bring the mass into solution in cold water, nearly neutralize as above, introduce sulphuretted hydrogen, and repeat the precipitation in the same manner as before. Finally filter, wash well with hot water, dry, ignite, and weigh the titanic oxide. In igniting the precipitate, it is well, after burning the filter, and igniting the precipitate, to cool the crucible a little, introduce some ammonium carbonate, heat moderately, until the

carbonate is volatilized, and then intensely, in order to expel the last traces of sulphuric acid.

Concentrate the filtrates and washings, after adding a little hydrochloric acid and potassium chlorate to about 200 c. c., precipitate ferric hydrate with ammonia, filter, wash well with hot water, dissolve the precipitate in hot dilute sulphuric acid, boil for some time to expel chlorine, add water, introduce into bottles, reduce with amalgamated zinc and platinum, and determine the iron by potassium permanganate, as directed in analysis of ammonia-iron-alum.

*Note 8.*—To *four fifths of filtrate (c)*, representing 4 gms. of ore, add a little potassium chlorate, and boil, to oxidize the ferrous oxide, nearly neutralize with sodium carbonate, add about 10 gms. of sodium acetate, and a few drops of acetic acid, dilute to 2.5 litres, in a large flask, and heat to boiling. Continue the boiling for about 5 minutes, remove the heat, allow the precipitate of basic acetates to settle, and filter as rapidly as possible, keeping the fluid hot while doing so. Should there be much manganese in an ore, it is well to dissolve the acetates in hydrochloric acid, and re-precipitate, by the same method, as in such a case, the acetates are apt to carry with them a small quantity of manganese, when the fluid contains much.

If the oxidation of the ferrous oxide, by boiling with potassium chlorate, has not been complete, the red modification of ferric oxide will be precipitated, giving a great deal of trouble, as it is apt to run through the filter, and is very insoluble. Generally, the danger can be detected in time to be avoided, by the appearance of the precipitate caused by the sodium carbonate, used in preparing the solution for the precipitation of acetates. If the oxidation of the ferrous oxide has been incomplete, the precipitate, instead of having the ordinary reddish-brown color, will be very dark (nearly black). In such a case, acidify with hydrochloric acid, add more potassium chlorate, boil for a short time, and precipitate the acetates as directed above.

*Note 9.*—Dissolve the basic acetates, or *precipitate (d)*, in nitric acid, by transferring the precipitate (a little at a time) from the filter to the acid, previously heated in a medium-sized beaker, stirring until the precipitate goes into solution. When all that can be conveniently removed from the filter is dissolved, warm the solution, and pour it back on the filter, to dissolve the portion adhering to it, and wash the filter thoroughly. Dilute the filtrate to 400 c. c., and divide into 2 portions, one of 300 c. c., for the determination of phosphoric acid, and another of 100 c. c., for that of alumina.

*Note 10.*—In *three fourths of solution of precipitate (d)*, containing 300 c. c., and representing 3 gms. of ore, determine phosphoric acid as directed in partial analysis of iron ore by first method.

*Note 11.*—In *one fourth of the solution of precipitate (d)*, containing 100 c. c., and representing 1 gm. of ore, precipitate the alumina, ferric hydrate, phosphoric acid, and titanio oxide together, by means of ammonia in excess. (See analysis of potassium alum.) From the percentage value of this precipitate, deduct that of ferric oxide, phosphoric acid, and titanio oxide, found elsewhere in the analysis. The difference will give the per cent of alumina.

A direct determination of the alumina may be made by fusing the ignited precipitate with acid sodium sulphate, digesting the fused mass with sulphuric acid, dissolving in water, adding an excess of pure potassium hydrate, and warming. By this means, the titanio oxide and the ferric oxide (carrying the phosphoric acid with it) will be precipitated, while the alumina will remain in solution. If, now, the solution be filtered, acidified with hydrochloric acid, and then made alkaline with ammonia, and boiled, the alumina will be precipitated, and can be determined. (Fres., *Quant. Anal.*, § 160, p. 361.) Or, fuse the ignited precipitate in a silver crucible with potassium hydrate, boil the mass with water, filter the alkaline fluid contain-

ing the alumina from the undissolved titanitic oxide, ferric oxide, and phosphoric acid, acidify the filtrate with hydrochloric acid, and precipitate the alumina with ammonium carbonate. (H. Rose, *Quant. Anal.*, chapter on Alumina, p. 149.)

*Note 12.*—Concentrate *filtrate* (*d*), or filtrate from the acetates, to 100 c. c., if possible, and precipitate the manganese, by adding a sufficient quantity of bromine, and heating. Filter out the manganese dioxide or *precipitate* (*f*), wash it moderately with hot water, transfer it with the filter (without drying) to a very small beaker, press down the filter upon the bottom of the beaker with a glass rod, add enough concentrated hydrochloric acid to cover the precipitate, and heat. When the manganese dioxide is dissolved, dilute with 20 or 30 c. c. of water, filter, and wash thoroughly. Heat the filtrate nearly to boiling, add excess of sodium carbonate, boil out free carbonic acid, filter out the manganese carbonate, wash with hot water, dry, ignite the carbonate to tri-mangano tetroxide, and calculate the sesquioxide. (See analysis of manganese ore.)

*Note 13.*—To *filtrate* (*f*) from the precipitate of manganese dioxide, add ammonia until it is slightly alkaline, then a sufficient quantity of ammonium oxalate. Boil, and allow the precipitate to settle completely. Pour the clear fluid through a filter, add to the precipitate 20 or 30 c. c. hot water, stir, and allow it to settle. Again pour the clear fluid through the filter. Then dissolve the precipitate in the beaker with hot dilute hydrochloric acid, add to the solution 4 or 5 c. c. of ammonium oxalate, and make it alkaline with ammonia. Finally, filter into a fresh beaker, and wash thoroughly with hot water. Dry the precipitate of calcium oxalate, transfer it to a weighed crucible, moisten it with concentrated sulphuric acid, evaporate off the excess of acid, ignite, and weigh the calcium sulphate, and calculate the per cent of lime. (Consult analysis of calcium carbonate.)

*Note 14.*—Concentrate the second filtrate, or the filtrate from the re-precipitated calcium oxalate to small bulk (after acidifying it with hydrochloric acid), make it alkaline with ammonia, and add it to the first filtrate from the calcium oxalate. (Consult analysis of limestone, and Fres., *Quant. Anal.*, § 154.6, p. 349.)

The combined filtrates constitute *filtrate (g)*. To this, if not already alkaline, add ammonia and a sufficient quantity of hydro-disodium phosphate, and allow to stand in the cold for some hours. When the precipitate of magnesium phosphate has entirely settled, filter, wash with dilute ammonia, dry, ignite, and weigh the magnesium pyrophosphate, and calculate the magnesia.

Owing to the quantity of ammonium chloride and other salts introduced into the analysis, by the re-agents used, it may be impossible to precipitate the magnesia completely. It is advisable, therefore, to treat the filtrate from the magnesium phosphate by one of the methods prescribed in the analysis of limestone, to recover any magnesia which may have been held in solution.

*Note. 15*—In iron ores containing titanium and requiring the use of sulphates, it is, of course, impossible to determine the sulphur in the current analysis. In such cases it is necessary to determine it in a separate portion of ore. A very good method of fusion for this purpose is one devised by Hart, for the decomposition of chromic iron ore (*Chem. Gaz.*, 1855, p. 458), and quoted by Fresenius, in his *Quantitative Analysis*, 4th London edition, § 160: "Fuse 8 parts of borax in a platinum crucible, add to the mass in fusion 1 part by weight of the finely pulverized ore, stir constantly, and keep the crucible half an hour longer at a bright red heat; add dry sodium carbonate as long as it causes effervescence, then gradually, and with frequent stirring with a platinum wire, 3 parts of a mixture of equal parts of potassium nitrate and sodium carbonate, and keep the mass a few minutes longer in fusion." Remove the mass from the crucible with water,

dissolve in hydrochloric acid, and determine sulphur, as in partial analysis of iron ore. (See note on p. 85.)

*Note 16.*—If zinc, nickel, and cobalt are present, they will be found in *filtrate* (*d*) (or the acetic acid solution, after removing the acetates), together with the manganese, lime, and magnesia. The best method for separating the nickel, cobalt, and zinc from the others, is that suggested by Gibbs, in the *Am. Jour. of Sci. and Arts*, Jan. 7, 1865: Add a few drops of acetic acid to the solution, boil, pass a rapid current of sulphuretted hydrogen for half an hour, and continue the boiling while doing so. Gibbs states that every trace of nickel, cobalt, and zinc will be precipitated as sulphides, while the whole of the manganese (as well as the lime and magnesia) remains in solution. These are to be determined as directed in notes 12, 13, and 14. If large quantities of manganese and zinc be present, as in the case of Franklinite ores, it is well to dissolve the precipitated sulphides, and after adding a sufficient quantity of sodium acetate and acetic acid, repeat the precipitation as above, as some manganese may be precipitated with the zinc. The writer has had it to occur in the analysis of Franklinite. Under ordinary circumstances, the re-precipitation is unnecessary. Dissolve the precipitated sulphides in aqua regia, convert the metals into double cyanides, by means of pure potassium cyanide, and precipitate the zinc by potassium sulphide, as recommended by Wöhler. (See analysis of German silver.) In the filtrate from the zinc, determine the nickel and cobalt as directed in the analysis of nickel ore.

*Note 17.*—Fuse 2 or 3 gms. of the ore with 10 times the weight of a mixture of equal parts of sodium carbonate and nitrate, extract the sodium arsenate by boiling with water, filter, acidulate the alkaline filtrate with hydrochloric acid, and precipitate the arsenic with sulphuretted hydrogen. Dissolve the sulphide by digesting with hydrochloric acid and potassium chlorate, make the solution



alkaline with ammonia, and determine the arsenic, as directed in the analysis of arsenic ore.

*Note 18.*—To determine sodium and potassium, fuse 1 gm. with precipitated calcium carbonate and ammonium chloride, and proceed as directed in analysis of feldspar, by J. Lawrence Smith's method.

*Note 19.*—If the ore contain copper in considerable quantity, it may be determined in *precipitate (c)*, or, if the quantity be very small, in a larger and separate portion of ore, by methods described in analysis of copper ore.

*Note 20.*—Water existing in the ore as mere hygroscopic moisture, is determined by drying 2 or 3 gms. of the finely powdered ore to constant weight at a temperature of about 110° C.

If the water be a constituent part of the ore, as in the case of limonite, determine it, as directed in analysis of hydro-disodium phosphate.

*Note 21.*—For the determination of chlorine, fluorine, carbonic acid, and organic matter, consult analysis of limestone.

*Appendix 1.*—Analysis of iron ore containing titanium, but no chromium:

Fuse 5 gms. of the finely powdered ore with 25 gms. of sodium carbonate, and 5 gms. of sodium nitrate, and treat the fused mass as directed in *Note 1*. Follow the directions given in the same note for effecting complete decomposition of the ore, and for filtering, washing, and drying *residue (a)*.

There will be a *solution (a)* and a *residue (a)*. Treat *residue (a)* as directed in *Note 2*. Omit the treatment of *solution (a)* with sodium carbonate and bromine, as directed in *Note 3*, pass sulphuretted hydrogen through *solution (a)*, and proceed as directed in *Note 5* for the treatment of the solution of *precipitate (b)*. The rest of the analysis is made in the same manner, as that of iron ores containing chromium as well as titanium.

*Appendix 2.*—Analysis of iron ore containing neither titanium nor chromium:

Fuse 5 gms. of the ore with sodium carbonate and nitrate, and proceed as directed in *Note 1* for the treatment of the fused mass. Probably, if the ore has been properly pulverized, there will be no undecomposed ore. Should there be any, dry and ignite the residue, and fuse it again with sodium carbonate and nitrate, and not with sulphate, as otherwise it will be necessary to determine the sulphur in a separate portion of ore.

There will be, as in the analysis of titaniferous iron ore containing chromium, a *solution (a)* and a *residue (a)*.

Dry, ignite, and weigh *residue (a)*, expel the silica with ammonium fluoride and sulphuric acid, and estimate the per cent of silica by the loss of weight. Should there be any residue left in the crucible, it will be entirely ferric oxide. Bring it into solution as directed in *Note 2*, by fusion with sodium sulphate. Divide this solution into 2 parts, one of one fifth, and another of four fifths. From the part containing one fifth, precipitate the ferric hydrate by ammonia, filter, dissolve the precipitate in sulphuric acid, and combine the solution with that of the ferric hydrate obtained from one fifth of *solution (a)*. Add the part containing four fifths to four fifths of *solution (a)*. Omit the treatment of *solution (a)* with sodium carbonate and bromine (as directed in *Note 3*), and at once divide it into two parts, one of one fifth for iron and sulphur, and another of four fifths for the determination of the other constituents of the ore. In the part containing one fifth, precipitate the ferric hydrate by ammonia, filter it out, dissolve it, together with the small precipitate obtained from one fifth of the residue left in the crucible after expelling silica, and determine the iron as usual, by titration with potassium permanganate. In the filtrate from the precipitate of ferric hydrate, in one fifth of *solution (a)*, determine the sulphur. (See partial analysis of iron ore.)

Through the portion of *solution (a)* containing four fifths (combined with four fourths of the solution of the residue left after expelling silica), pass sulphuretted hydrogen. (See *Note 5*.) Then oxidize the filtrate, and

proceed as directed in *Note 8*. After this, continue the analysis, as directed for that ore, containing both chromium and titanium.

*Appendix 3*.—Vanadium and tungsten have been found in iron ores.

To determine vanadium, fuse 15 or 20 gms. of the ore, in the form of impalpable powder, with one third its weight of potassium nitrate. Then cool, and remove the mass from the crucible by digesting with water as usual, and mix carefully with nitric acid, leaving the solution slightly alkaline. Filter, and add to the filtrate barium chloride as long as it produces a precipitate. Filter out the baryta salts; to the still moist precipitate add dilute sulphuric acid in slight excess, boil and filter. Then neutralize the filtrate with ammonia, concentrate, and add a fragment of ammonium chloride. As the ammonium chloride dissolves, ammonium vanadate is precipitated, as a crystalline powder. Allow it to settle, filter it out, and wash it with solution of ammonium chloride. Dry the precipitate, and heat it to red vanadic acid, which fuses, and cools to a crystalline mass. (H. Rose, *Quant. Anal.*, pp. 498, *et seq.*)

To determine tungsten, fuse 15 or 20 gms. of the finely pulverized ore with four times its weight of sodium carbonate. (Do not use nitrate.) Digest the fused mass with water, filter, and wash. Saturate the solution carefully with nitric acid, so that it will slightly redden litmus paper, after the carbonic acid has been expelled. Let it stand 24 hours in a moderately warm place, and then, but not before, add solution of mercurous nitrate as long as it produces a precipitate. Let the precipitate settle, collect it on a filter, and wash with water, to which has been added a little mercurous nitrate. This is necessary to prevent the liquor from running through the filter turbid. After drying, burn the precipitate under a chimney with a good draught. After calcination, tungstic acid remains pure. Repeat the ignition to constant weight. (See H. Rose, *Quant. Anal.*, p. 488.)

## CHAPTER XVI.

### SLAG.

Fuse 5 gms. of the finely-pulverized slag with 25 gms. of anhydrous sodium carbonate and 2 gms. of sodium nitrate, and proceed to the determination of the silica, as in the analysis of feldspar.

Dilute the filtrate from the silica, with water, to 500 c. c., and divide it into 2 portions, one of 100 c. c., and equivalent to 1 gm. of the slag; the other of 400 c. c., and equivalent to 4 gms.

In the portion containing 100 c. c., precipitate the ferric oxide with ammonia, filter and wash out all sulphuric acid, dissolve the precipitate in hot dilute sulphuric acid, transfer to bottles, reduce with zinc and platinum, titrate with standardized potassium permanganate, determine the iron and calculate it to ferrous oxide. Acidify the filtrate from the precipitate of ferric oxide slightly with hydrochloric acid, and determine the sulphur, as in the analysis of magnesium sulphate.

Saturate the portion containing 400 c. c. with sulphuretted hydrogen, filter, wash well with water, and determine any metals that may be present, by the methods given in their respective analyses, with the exception of platinum, a small quantity of which may be introduced into the analysis by the action of the fluxes on the crucible.

Boil the filtrate from the precipitate produced by sulphuretted hydrogen, with about 0.500 gm. of potassium chlorate, to oxidize sulphur of the sulphuretted hydrogen, and raise the ferrous to ferric oxide, and continue to boil until free chlorine is expelled. Then add saturated solution of sodium carbonate until the fluid is slightly alkaline, acidify it with acetic acid, and boil to precipitate

basic acetates. (See analysis of manganese ore.) Heat 15 or 20 c. c. of nitric acid in a beaker, and by means of a spatula add to it the precipitate of acetates (a little at a time), with frequent stirring. When all that can be conveniently reached by the spatula is removed, pour the hot solution through the filter, and wash it well. Dilute the solution to 400 c. c., and divide it into 2 portions, one of 100 c. c., and the other of 300.

In the portion containing 300 c. c., and equivalent to 3 gms. of slag, determine the phosphoric acid, as in analysis of iron ore by the first method, if the quantity of iron present be small, or by the second method, if it be large.

In the portion containing 100 c. c., and equivalent to 1 gm. of slag, precipitate alumina, ferric oxide, and phosphoric acid together, by means of ammonia, and proceed as in the analysis of potassium alum.

From the weight of this precipitate, after ignition, deduct the sum of the weights of phosphoric acid and ferric oxide, found previously. The difference will be the weight of the alumina.

Concentrate the filtrate from the basic acetates to small volume, precipitate with bromine, and determine the manganese as in the analysis of manganese ore. Calculate the manganese to manganous oxide.

In the filtrate from the precipitate of manganic oxide, determine the lime and magnesia as in the analysis of limestone.

Determine alkalis as in the analysis of feldspar.

## CHAPTER XVII.

### CAST-IRON, STEEL, AND WROUGHT-IRON.

The analysis of cast-iron covers the ground entirely, as the constituents of steel and wrought-iron are determined in the same manner as those of cast-iron. A large number of substances may be found in the iron, either combined or mixed with it. Those usually determined in cast-iron are combined carbon (or carbon chemically combined with iron), uncombined carbon (or carbon existing in the form of graphite), silicon, phosphorus, sulphur, manganese, and copper. Besides these, the iron may contain nitrogen, potassium, sodium, lithium, calcium, magnesium, aluminium, chromium, titanium, zinc, cobalt, nickel, tin, arsenic, antimony, vanadium, molybdenum, barium, slag, and, in rare cases, traces of other metals. Iron is usually estimated by difference, that is, the difference between 100 and the sum of the per cents of the other substances found. In many cases, however, it is necessary to determine it directly. Owing to the large number of substances that may be found in cast-iron, it is better to make the analysis on a number of separate portions, to avoid complexity.

For the determination of *iron*, *barium*, and *titanium*, weigh 10 gms. of the material in the form of borings, filings, or chips, transfer to a capacious casserole, cover with a convex glass, add 300 c. c. of water, containing 30 c. c. of concentrated sulphuric acid, heat on a water-bath until the iron is dissolved, remove the cover, and heat over a burner until copious fumes of sulphuric acid are evolved. Cool, dilute with about 200 c. c. of cold water, filter, and wash with about the same quantity of cold water. Dry the residue (which may contain graphitic carbon, iron, barium, and titanium, besides silica), ignite

it, together with the filter, in a platinum crucible, add 7 or 8 gms. of sodium carbonate and 3 or 4 of sodium nitrate, and fuse over a Bunsen burner, until the contents of the crucible are fluid. By this means the carbon will be consumed. Then remove the fused mass from the crucible with water, acidulate with hydrochloric acid, add 8 or 10 drops of sulphuric acid, and evaporate to dryness, as usual, for silica. To the dry mass add about 1 c. c. of concentrated sulphuric acid, and 40 or 50 c. c. of water, filter out and thoroughly wash the silica, which may contain barium sulphate and titanic oxide, and add the filtrate to the principal solution, which will now contain all the iron and the larger part of the titanium. Dry the siliceous residue, treat it with acid sodium sulphate and sulphuric acid, as directed in "complete analysis of iron ore," *Note 2*, dissolve in cold water, filter, wash thoroughly with cold water, and add the filtrate to the principal solution, which will now contain all the iron and titanium, while the residue will contain silica and barium. Dry the residue, ignite it in a platinum crucible, cool, and weigh. Expel the silica with ammonium fluoride and sulphuric acid. The loss will be silica. Determine it as a check. Fuse the residue with sodium carbonate, digest the fused mass with hot water, transfer it to a filter, and wash with hot water, until the sodium sulphate and excess of flux is washed out. The barium will remain on the filter as carbonate. Dissolve it through the filter with dilute hydrochloric acid, precipitate barium sulphate as usual, and calculate the barium.

Precipitate the ferric and titanic oxides with pure potassium hydrate, and proceed to determine the titanium as directed in *Note 7* of "complete analysis of iron ore."

Treat the filtrate as directed in the same note, and in one tenth determine the iron by titration with potassium permanganate, as usual.

If no titanium be present, the determination of iron may be made on 1 gm., which is to be treated in the man-

ner directed above, with the exception of the steps taken for the separation of titanium. Of course, the treatment for the determination of barium will be unnecessary.

The presence of hydrocarbons in the solution renders it impossible to determine iron accurately with potassium permanganate. Consequently, it is advisable, even after evaporating to fumes of  $\text{SO}_3$ , as above, to precipitate the ferric hydrate, wash it well, and re-dissolve it in sulphuric acid.

A great many methods for the determination of carbon in iron and steel have been proposed and used, of which only a few can be noticed here. Usually, all that is required to be known is the total amount of carbon. In iron and steel containing no graphite this is all combined.

Where the per cent of carbon present in both conditions (that is, as combined with the iron as carbide and uncombined or graphitic) is required, the total carbon is determined in one portion of the iron, and the graphite in another. The difference between the amount of total carbon, and that of the graphite, gives the amount of combined carbon.

To determine total carbon, Weyl dissolves a piece of the iron, previously weighed, suspended in dilute hydrochloric acid, by means of platinum pincers, or wire, from the positive pole of a weak galvanic battery (1 Bunsen element), the platinum foil forming the negative electrode being also immersed in the fluid. The strength of the current is regulated by increasing or diminishing the distance between the piece of iron or steel and the platinum foil, which form the two electrodes. No ferric chloride should be formed. Should it be, it can be detected by the yellowish color of the solution descending from the iron. To prevent this, the distance between the electrodes is increased. When a sufficient quantity of the iron has been dissolved, which will require 10 or 12 hours, the carbon is removed from the undissolved portion of the iron, by brushing it off and washing it into the solution. The lump

*1.1.1. Carbon*



of iron is then dried and weighed, and the quantity taken determined by the loss of weight. The carbon is then collected in a funnel, the neck of which is lightly plugged with a little ignited asbestos, washed moderately with water, dried, mixed with copper oxide, and burned in a current of oxygen gas. The resulting carbonic acid is absorbed in soda-lime, and the carbon calculated. (See Fres., *Quant. Anal.*, § 229, p. 536, and also Crookes's *Select Methods*, p. 76.) For the method of making the combustion, see "Sugar (Ultimate Analysis)."

Weyl's method is applicable to the determination of carbon in hard iron, that cannot be readily broken into small fragments, or be reduced to powder, by the drill or file. As carbon is sometimes carried by the mechanical working of the current, particularly in the case of steel, from the positive to the negative electrode, it is prudent to interpose a diaphragm of bladder or parchment paper.

Regnault's method, for which consult Fres., *Quant. Anal.*, 4th London Ed., § 249; and Boussingault's, for which see Crookes's *Select Methods*, p. 77, can be used only in the case of iron that is susceptible of being reduced to a state of very fine division.

R. E. Rogers and Wm. B. Rogers proposed the use of copper sulphate to dissolve the iron, and the oxidation of the residual carbon by means of potassium bichromate and sulphuric acid, absorbing the resulting carbonic acid in soda-lime or potassium hydrate. (See *Am. Jour. Sci. and Arts*, 1848.)

Ullgren afterward proposed the same method, using chromic acid instead of potassium bichromate. (See Fres., *Quant. Anal.*, 4th London Ed., § 249.)

In a paper published in the *Chemical News* of May, 1869, Arthur Elliott proposed a modification of Rogers's and Ullgren's methods. His process is among the best in use. It has given very satisfactory results, in a great many analyses, made by the writer, of iron, steel, graphite, and coal of various kinds. For a few experi-

ments, giving the time occupied and the per cent of carbon obtained, by this method, and combustion in oxygen, see a paper published by the writer in the *Am. Chemist* of October, 1871.

*Total*  
*Calc.*

Add to 2 or 3 gms. of borings, filings, or very small fragments (in a small beaker) 50 c. c. of a solution of neutral copper sulphate (containing 1 part of the salt in 5 parts of water), and heat gently for about ten minutes. In order to obtain the neutral sulphate, dissolve the recrystallized salt (as sold by the dealers) in water, add a small quantity of copper oxide, boil until the copper sulphate begins to crystallize, filter out the excess of oxide, and concentrate the solution until it is completely crystallized. Dry the crystals by draining off the water, should there be any, and pressing them between layers of bibulous paper, and dissolve them in water in the proportion stated above. After heating the solution of copper sulphate, containing the iron, about ten minutes, by which means the iron will be dissolved and copper precipitated, add 20 c. c. of a solution of copper chloride (containing 1 part of the salt in 2 parts of water), and 50 c. c. of concentrated hydrochloric acid, and heat to a point just below boiling, with frequent stirring, until the precipitated copper is dissolved, leaving the carbon free. Filter it out through a funnel, made of large glass tubing. The funnel should be about half an inch in diameter, and 5 inches long, and drawn at one end, to a point about 4 mm. wide. Fill the point of the funnel with broken glass, up to the shoulder, and place upon the glass a thin layer of ignited asbestos, pressing it carefully against the walls of the funnel. Care should be taken not to make the plug of asbestos too thick or compact, as it is liable to become clogged by the carbon. The layer of asbestos should be thin enough to allow water to run through at the rate of a funnelful in ten seconds. Transfer the carbon to the filter, and wash with hot water until it is free from chlorides. After washing down all the carbon from the sides of the

tube, cut it off about 1 inch above the layer of carbon, by scratching the glass with a file, and pressing a red-hot glass rod against the cut. Then invert the part containing the carbon into the mouth of the decomposing flask of an apparatus similar to that described in the analysis of calcite, for the determination of carbonic acid by direct weight, and blow the contents into the flask, avoiding the use of water by wiping out any carbon that may adhere to the glass with a little ignited asbestos, and throwing this also into the flask. To the filtrate from the carbon add 4 or 5 c. c. of concentrated hydrochloric acid (to prevent the formation of any precipitate of basic copper salt), and dilute with water, until the fluid is transparent. If any carbon has passed through the asbestos it can readily be seen in the transparent fluid. Should there be any, allow it to settle, filter it out on another filter of ignited asbestos, and add it to that in the flask. Then weigh the absorption-tube, introduce into the flask about 3 gms. of chromic acid, put the apparatus together, and start the aspirator very slowly. After the aspirator has run long enough to partially exhaust the air in the apparatus, introduce, through the funnel-tube, about 30 c. c. of pure concentrated sulphuric acid, close the stop-cock of the funnel-tube, and heat slowly up to boiling. After the acid boils, remove the heat, put on the guard tube, open the stop-cock of the funnel-tube, and aspirate slowly, until the absorption-tube is cool. After it is thoroughly cooled, weigh it, and from the increase of weight, due to carbonic acid, calculate the carbon, (For Elliott's description, consult A. Vacher's 5th Edition of *Fres. Quant. Anal.*, London, 1870.) (See cut on p. 25.)

Professor Langley proposes to burn the carbon directly in a current of oxygen, after treating the iron with copper sulphate. His directions are to introduce the iron or steel in a finely-divided condition into the cold solution of copper sulphate, and raise the heat gradually, on a water-bath, to 80° C., with frequent stirring, and filter the

spongy mass on a common funnel, loosely plugged with asbestos. A porcelain tube of about three fourths of an inch internal diameter is placed in a furnace, which will keep at least 10 inches of the tube up to a full yellow heat; a plug 2 inches in length is inserted in the anterior end. This plug is made by coiling up fine copper bell-wire till it is just large enough to fill the tube closely; the interstices between the wires will always be large enough to allow of the passage of gas. Air being now drawn through the apparatus, the copper is deeply oxidized, and thus a filter of oxide of copper is produced, which, at a red heat, will oxidize any carbonic oxide or hydrocarbon which may pass over it. To hold the matter to be burned, a copper boat is provided, which is easily made by folding up a piece of sheet copper; it should be about 5 inches long, and, when bent, form a half cylinder with closed ends; a few small holes may be made through the bottom with a punch, in order to make the vessel porous. On the bottom of the boat a stratum of asbestos is laid, and on this the mixed copper and carbon sponge is loosely placed. The anterior end of the tube containing the wire plug being first heated, the boat is then introduced, and the combustion conducted in the usual manner, either in purified oxygen or air. (See *Am. Chem.*, Vol. VI., September, 1875.)

Carbon  
Dr. Eggertz, of the Swedish School of Mines, has proposed a method of determining the combined carbon in iron and steel, by comparing the color of a solution of the iron or steel under examination with that of a solution of another sample of known constitution. When steel or pig-iron, containing carbon in chemical combination, is dissolved in nitric acid, a soluble brown coloring matter is formed, whose coloring power is very intense, and the solution assumes a tint which is dark in proportion to the quantity of the chemically combined carbon. Iron and graphite do not influence this coloration, for the solution of ferrous nitrate is colorless, or, at most, slightly green-

ish, unless extremely concentrated, and graphite is insoluble in nitric acid. Thus, in dissolving two pieces of different steels, of the same weight, in nitric acid, taking care to dilute the dark solution until the two liquids present exactly the same color, it is very evident that the more highly carburetted steel will furnish the larger quantity of liquid, and that the proportion of the volumes will indicate the relative proportion of color in the two steels. If, now, the composition and per cent of carbon of one of the steels is known, the absolute percentage of carbon in the other steel may be immediately deduced. Dr. Eggertz has applied these reactions to a method of estimating the combined carbon. In a cylindrical test-tube, dissolve gradually in the cold 10 centigrammes of wrought-iron, steel, or cast-iron, reduced to a fine powder, in  $1\frac{1}{2}$  to 5 c. c. of nitric acid of 1.2 sp. gr. The nitric must contain no hydrochloric acid, because the solution of iron would have a yellow tint. In proportion as the metal contains more carbon, more nitric acid must be used. After some time, when the chief part of the metal appears to be attacked, place the tube in a water-bath, and warm it to  $80^{\circ}$  C., in such a position that only the lower part of the tube is in contact with warm water; a movement takes place in the acid which favors its reaction upon the metal; a slight disengagement of gas from all the particles of carbon may be observed. The operation should always be conducted under the same conditions as to heat and length of time. The evolution of gas having ceased (in operating upon steel, the reaction must continue two or three hours), place the tubes in a large vessel filled with cold-water, to bring the solution always to the same temperature. This precaution is indispensable, because the same liquid is darker when warm than when cold. Afterward, pour off, as exactly as possible, the clear liquid into a graduated burette. Upon the black residue remaining in the tube, pour some drops of nitric acid, and heat carefully over a lamp. If there is no further liberation of gas, the residue

consists of nothing but graphite or silica. Cool the new solution, and add it to that which is already in the burette. The liquid is then diluted with water until its color corresponds exactly with that of the normal liquid, which latter should be of such a degree of concentration that each c. c. represents 0.0001 gm. of carbon. If, for instance, this normal liquid is prepared from cast-steel containing exactly 0.85 per cent of carbon, 1 decigramme of that steel must be dissolved in 8.5 c. c. of nitric acid; 100 gms. of steel, containing 85 centigrammes of carbon, would thus be dissolved in 8500 c. c. of the normal solution; 100 c. c. of that solution would represent 1 centigramme of carbon, and, consequently, 1 c. c. of the normal solution would represent 0.0001 gm. of carbon.

To compare the normal solution with the solution of iron under examination, it should be contained in a tube of the same kind, and when the two tubes are held together by daylight before a thin sheet of paper, the color should be exactly the same in both of them. As the normal solution alters slightly in color by keeping, and begins to become paler after 24 hours, it is not possible to keep such a solution for use in a tube hermetically sealed. A solution of burnt sugar in weak alcohol gives a solution of exactly the same shade of color as the normal solution, and maintains its color for a considerable time when protected from the light. A solution of roasted coffee in alcohol has also been found to be very satisfactory. But the best plan is to make the solution fresh, as it is required, by dissolving 0.1 gm. of steel, containing a known amount of carbon, in 5 c. c. of nitric acid, and diluting it to the requisite degree, which may be indicated by a mark upon the tube corresponding to the percentage of carbon in the steel. If an iron solution of exactly the same color as the normal solution is diluted with one tenth of its bulk of water, the color becomes distinctly paler, so that the delicacy of the method may be judged of from this.

J. Blodgett Britton, in the *Jour. of the Franklin Insti-*

*tute* for May, 1870, has suggested a modification. Instead of a single tube, containing a standard solution for comparison, a number of tubes, having their solutions differently standardized one from the other, are employed. They are arranged securely in a wooden frame, with spaces between for placing the tube containing the solution to be tested. The tubes are five eighths of an inch in diameter, and three and a half inches in length, filled with water and alcohol, colored with roasted coffee, and hermetically sealed. The solution in the first tube has its color to correspond exactly with one produced by 1 gm. of iron containing 0.02 per cent of combined carbon, dissolved in 15 c. c. of nitric acid. The solution in the tube next to it has its color to correspond with one produced by the same quantity of iron, but containing 0.04 per cent of combined carbon, and so with each of the other tubes, increasing 0.02 per cent of carbon in regular succession, the last reaching 0.3 per cent, which is indicated by figures on the rail of the frame opposite each tube. On the back of the instrument is stretched some fine white parchment paper.

The process is conducted as follows :

One gm. of the finely-divided metal is put into a tube of about 1.5 inches in diameter and 10 inches long, and digested for 15 or 20 minutes in 10 c. c. of nitric acid of a little more than 1.2 sp. gr., free from chlorine. The solution is then cautiously poured into a beaker, and a small portion of metal, which remains undissolved and adheres to the bottom of the tube, is treated with 5 c. c. of fresh acid, exposed to a gentle heat till completely dissolved, and added to the other. The contents of the beaker, when sufficiently cool, are filtered through two thicknesses of German paper (not previously moistened, and of a diameter not exceeding 4.5 inches) into a tube about five inches long, and of precisely the same diameter as those in the instrument. After the filtered solution has remained for some minutes at the temperature of the atmo-

sphere, and its color become fixed, the tube is placed in the instrument, and the carbon determined by a comparison of shades; the determination may be made readily as closely as 0.01 per cent. Heat should not be applied in the first instance to facilitate the solution of the metal, because a high temperature is apt to cause a slight change of color. Two thicknesses of paper are taken because one is liable to break, and the paper should be used dry, for, if previously wetted, the water will weaken the color of the solution, and it ought to be cut to a size not exceeding 4.5 inches, to prevent undue absorption.

If the metal to be examined contains more than 0.3 per cent of carbon, 0.5 gm., or less, of it may be taken, or the solution may be diluted with an equal volume of water, or more, and the proper allowance made; or an instrument of higher range may be used. On the other hand, if the metal contains a very small percentage of carbon, 2 gms. of it may be taken. (Compare Crookes's *Select Methods*, p. 81.)

For other methods, consult Fres., *Quant. Anal.*, 4th London Ed., § 249.

Carbon { For the determination of the graphite Eggertz's method is as follows: One gramme or more of iron, reduced to small pieces, or white pig-iron crushed in a steel mortar, or gray pig-iron in small chips, is dissolved in 15 c. c. of hydrochloric acid of 1.12 density, in a small flask covered with a watch-glass, and, when the iron is dissolved, the solution boiled for half an hour. All the carbon combined with the iron is disengaged in the form of carburetted hydrogen gas, while the graphite and silica remain. If the carbonaceous residue, left after dissolving the iron, comes in contact with atmospheric air before the liquid is boiled, it is so altered that it is not dissolved, and disengaged as gas. The graphite that remains after boiling the liquid is collected on a filter of known weight, washed, dried, and weighed. It is then burnt, and the residual silica weighed to ascertain the weight of graphite. See Crookes's *Select*



*Methods*, pp. 79 and 80, where a modification is proposed, as follows:

In a beaker of 100 c. c. capacity, mix 4 c. c. of sulphuric acid and 20 c. c. of water, and when the heat produced by the combination of the water and the acid has entirely disappeared, shake 2 gms. of finely powdered pig-iron into the dilute acid, and boil for half an hour. (For steel and wrought-iron not less than 3 gms. should be taken, and the acid for solution increased in proportion.) The solution is then evaporated until it measures 18 c. c., allowed to cool to the temperature of 50° C., and 4 c. c. of nitric acid of sp. gr. 1.20 added; boil for a quarter of an hour, and allow to evaporate on a water-bath until, on holding a watch-glass over the beaker, there occurs upon it no perceptible condensation. To the dry mass add 30 c. c. of water, and 5 c. c. of hydrochloric acid, sp. gr. 1.16, boil for a quarter of an hour, and add more hydrochloric acid if there appears to be anything besides silica and graphite undissolved. The insoluble silica and graphite are thrown on a filter (which has been dried at 100° C. and carefully weighed), washed with cold water until the washings give no reaction for iron when tested with potassium ferrocyanide, then washed with boiling water containing 5 per cent of nitric acid. The silica and graphite are then dried on the filter at 100° C., and weighed, ignited in a porcelain crucible, and the weight carefully taken. The difference between the weighings before and after ignition gives the amount of the graphite.

The objection to the method of determining the graphite by burning it, after drying it at 100° C., when mixed with silica, is that at that temperature water is not expelled from the silica, or even at a much higher heat. Consequently, the loss which represents the weight of graphite is partly water. This objection applies to all methods where the graphite is determined by igniting and weighing the residual silica. The extreme difficulty, at times, of burning

the graphite in a crucible may be considered another objection.

The best method is to dissolve from 2 to 3 gms. of gray pig-iron, or from 4 to 5 gms. of white iron, steel, or wrought-iron in dilute hydrochloric acid, and boil for about half an hour, filter through asbestos in a funnel made of glass tubing, and arranged as directed for the determination of total carbon; wash with hot water until all acid is washed out, then with strong solution of potassium hydrate, which will remove silica, afterward with hot water, to wash out any potassium carbonate, of which the potassium hydrate is apt to contain some, then with alcohol (which will remove hydrocarbons) until the alcohol runs through the funnel colorless, again with a little hot water, then with ether until it passes through colorless, in order to displace the water, and remove another class of hydrocarbons, which the alcohol may have failed to reach. It is well, finally, to wash with a little hot water (particularly if the ether used is not perfectly pure), in order to keep the graphite from adhering to the walls of the funnel, when blown into the decomposing-flask, being careful to remove any excess of water by gently blowing through the funnel. After the graphite is thoroughly washed, it is transferred to the decomposing-flask, and oxidized with chromic and sulphuric acids, in precisely the same manner as in the determination of total carbon. If it is preferred, the graphite may be transferred to a boat, and burned in a current of oxygen as in "Sugar (Ultimate Analysis)."

Si  
S  
P  
To determine the silicon, sulphur, and phosphorus, dissolve 10 gms. of potassium chlorate in 200 c. c. of hot water, in a flask holding at least 1 litre, heat to boiling, and introduce 5 gms. of the iron, in the form of borings or chips. Then remove the source of heat, add (little by little) 60 c. c. of pure concentrated hydrochloric acid, and heat until the iron is dissolved, which may be known by there being no heavy particles on the bottom of the flask,

which will not rise when the flask is shaken. There may be a large quantity of black carbon in the fluid, but this will rise when agitated. Transfer the contents of the flask to a large casserole, evaporate to dryness on a water-bath, and then heat in an air-bath, at about  $110^{\circ}\text{C}$ ., until the odor of hydrochloric acid cannot be detected. To the thoroughly dry mass add 10 c. c. of hydrochloric acid, and 30 c. c. of water, and heat on a water-bath until everything is dissolved except silica and graphite. Then dilute with 50 or 60 c. c. of water, filter, and wash with cold water, until the washings give no reaction for chlorine. To the filtrate add ammonia in excess, to precipitate the ferric hydrate, which will carry the phosphorus with it, and wash until the washings give no reaction for sulphuric acid. Acidulate the filtrate slightly with hydrochloric acid, precipitate barium sulphate as usual, and calculate the sulphur. In almost all cases, 2 c. c. of a saturated solution of barium chloride will be sufficient to precipitate all the sulphur in 5 gms. of iron. It is well, however, to be assured that a sufficient quantity of the reagent has been added, by testing a few drops of the filtrate with sulphuric acid, as directed in the analysis of magnesium sulphate.

To determine the phosphorus, dissolve the precipitate of ferric hydrate, containing ferric phosphate, in hydrochloric acid, and proceed as directed in partial analysis of iron ore by *Method No. 2*.

To determine the silicon, dry the residue (containing silica, graphite, and perhaps a little ferric oxide) left after filtering the solution of 5 gms. of iron, burn it in a platinum crucible, add 5 or 6 gms. of sodium carbonate, and 2 or 3 gms. of sodium nitrate, and heat over a good burner until the contents of the crucible are fluid and the graphite oxidized. Do not heat unnecessarily. Treat the fused mass as directed in the analysis of feldspar for the determination of silica. As the silica obtained may contain a little ferric oxide and platinum from the crucible, expel it

by means of hydrofluoric and sulphuric acids, and from the loss calculate the silicon. The estimation of the silicon by treating the original residue with hydrofluoric and sulphuric acids, before removing the graphite, would be erroneous, as some of the graphite would also be expelled by the action of the acids. Such has been the experience of the writer.

A common method of determining sulphur in iron is to dissolve a weighed quantity of the iron with hydrochloric acid in a flask or retort, conducting the sulphuretted hydrogen formed into a solution containing some metal, which will be precipitated as sulphide, oxidizing the sulphur of the sulphide into sulphuric acid, and precipitating it with barium chloride. Dr. Drown has substituted a solution of potassium permanganate. By his method, 5 or 6 gms. of the iron are dissolved in hydrochloric acid, and the sulphuretted hydrogen resulting conducted into a solution of 1 gm. of potassium permanganate in 200 c. c. of water, contained in three tubes or bottles. After the evolution of the gas has entirely ceased, and air has been drawn through the tubes or bottles for some time, the contents are poured into a beaker, and the bottles rinsed out with water, and any manganese oxide dissolved in a little hydrochloric acid. Enough hydrochloric acid is then added to the beaker to completely decompose the permanganate and convert it into a clear, colorless solution, in which the sulphuric acid may be directly precipitated. If the solution does not become perfectly clear, owing to impurities in the permanganate used, filtration is necessary before precipitation. Before precipitating the sulphuric acid, the residue left after treatment with hydrochloric acid in the flask is filtered off and washed, then evaporated twice to dryness with aqua regia, taken up with hydrochloric acid, filtered, and the filtrate added to the main solution. (See *Am. Chemist*, Vol. IV., May, 1874.)

For a colorimetric method of estimating sulphur in iron by Eggertz, see Crookes's *Select Methods*, p. 85.

For the determination of chromium, aluminum, manganese, zinc, nickel, cobalt, calcium, and magnesium, dissolve 5 gms. of iron or steel, in the same manner as for the determination of silicon, sulphur, and phosphorus, with hydrochloric acid and potassium chlorate, and after evaporating, drying, dissolving the mass, and filtering out the silica (which may be determined here, as a check on the previous determination), proceed as directed in *Notes* 3 and 4 of "Complete Analysis of Iron Ore" for the determination of *chromium*, and the treatment of residues and precipitates.

C  
al  
Mn  
Zn  
Ca  
Mg

Dissolve the precipitate caused by sodium carbonate, in the treatment for chromium, in hydrochloric acid, add to it the solution of any residue, and precipitate, as directed in *Note* 4 of "Complete Analysis of Iron Ore," and boil with the addition of 2 or 3 c. c. of nitric acid, to ensure complete oxidation of iron. Then precipitate basic acetates twice, as directed in the analysis of manganese ore, filter, and wash well.

In the filtrate from the basic acetates will be found the manganese, zinc, nickel, cobalt, calcium, and magnesium. For their separation and determination, consult *Note* 16 of "Complete Analysis of Iron Ore."

If no zinc, nickel, or cobalt be present, the manganese may be precipitated by bromine, and determined immediately, as directed in *Note* 12 of "Complete Analysis of Iron Ore," and the calcium and magnesium determined in the filtrate from the manganese as in *Notes* 13 and 14.

To determine the aluminum, dry the precipitated acetates, transfer them to a silver crucible, burn the filter, add the ash, and fuse with pure sodium or potassium hydrate; then boil the fused mass with water. By this means, the alumina will be dissolved. Filter, wash, acidify the alkaline filtrate strongly with hydrochloric acid, add slight excess of ammonia, and determine the alumina as in the analysis of potash alum, from which calculate the *aluminum*. H. Rose, who suggested the fusion with po-

al

tassium hydrate, precipitates the alumina with ammonium carbonate, from the solution, strongly acidified with hydrochloric acid. (See his *Quant. Anal.*, "Separation of Alumina from Ferric Oxide.")

To determine copper, tin, arsenic, and antimony, treat 20 gms. of the iron in the finest possible state of division with a previously-heated mixture of 1 volume of nitric acid and 3 volumes of hydrochloric acid (both acids must be pure and strong) in a very capacious, long-necked, obliquely placed flask, at a gentle heat. When all visible action has ceased, decant the solution, and treat the residue with a fresh portion of aqua regia. Mix the solutions, dilute copiously, and treat in a large flask with sulphuretted hydrogen, at first in the cold, then at 70° C. Allow the fluid (saturated with sulphuretted hydrogen) to settle for 24 hours, filter, dry the precipitate, which consists principally of sulphur, and extract it with bisulphide of carbon. There usually remains a small black residue, which often contains, besides sulphide of copper, a little sulphide of arsenic and sulphide of antimony. (See *Fres., Quant. Anal.*, § 249-5.) There may be also sulphides of other metals of Groups V. and VI. Filter out the precipitated sulphides, wash and digest the precipitate with potassium hydrate and potassium sulphide containing an excess of sulphur. The copper sulphide will remain undissolved while the sulphides of tin, antimony, and arsenic will go into solution. Decompose the copper sulphide with nitric acid, replace the nitric with sulphuric acid, and determine the copper electrolytically, as in the analysis of copper ore.

For the determination of the tin, arsenic, and antimony, consult analysis of type metal.

To determine the alkaline metals, dissolve 20 gms. of the iron in dilute hydrochloric acid, evaporate nearly to dryness, on a water-bath, in order to remove large excess of free acid, add water, and boil. Add to the solution an excess of barium hydrate, and proceed as in the analysis of feldspar.

To determine the nitrogen, treat about 2 gms. of the finely-divided cast-iron, in a tubulated retort, with a solution of 10 gms. of neutral crystallized copper sulphate, and 6 gms. of fused sodium chloride. When the iron is dissolved, add milk of lime, and distill, until half the fluid has passed over into a receiver which contains a sufficient amount of standard solution of sulphuric acid, and determine the amount of sulphuric acid neutralized by the ammonia, which has been expelled, by titration with standard solution of potash, as in the analysis of guano (which consult; also see Fres., *Quant. Anal.*, § 249, 4th London Edition). For a description of the apparatus, and the method of making the distillation, consult Fres., *Quant. Anal.*, § 99—3—a., p. 157. The ammonia is calculated to nitrogen. Thorpe suggests that the nitrogen, if minute in quantity, may be determined by Nessler's solution. (See analysis of potable water.) Only a part of the nitrogen is evolved by this treatment; the rest remains in the carbonaceous residue. Ullgren determines this by combustion with mercuric sulphate, and measurement of the evolved nitrogen. The apparatus consists of an ordinary combustion-tube, about 30 c. c. long, one end of which is closed by fusion. It is then filled for about 5 c. c. with magnesite or sodium bicarbonate, on which is placed a plug of asbestos. A mixture of about 0.1 gm. of the carbonaceous residue (previously dried at 130° C.), and 3.5 or 4 gms. of mercuric sulphate, is then made in an agate mortar, and transferred to the tube, together with a small quantity of mercuric sulphate, used to rinse the mortar. An asbestos plug follows next; then, for about one third of the remainder of the tube, a layer of pumice, mixed with moistened mercuric sulphate and dried; on this is placed a plug of asbestos. Finally, the tube is filled with pumice, which has been boiled in a concentrated solution of potassium bichromate, and allowed to drain. This serves to absorb the sulphur dioxide which may be formed. The tube is then closed with a caoutchouc stopper, through

which passes a small tube, so bent that it passes down into a mercury trough, and up under a vertical tube holding about 90 c. c., having a bulb of a capacity of about 40 c. c. blown in it, in such a way that the part above the bulb will hold about 20 c. c., and the part below the bulb about 30 c. c. The narrower part is graduated to divisions of 0.1 c. c. The tube is filled with mercury, and inverted in the bath. Solution of potassium hydrate (1 part potassium hydrate and 2 parts water) is introduced until the bulb is filled to within about 10 c. c., and then 15 c. c. of a saturated and clear solution of tannic acid. The extreme end of the tube, where the magnesite is placed, is now heated gently, the heat being gradually extended and increased until about half the carbonate is decomposed, thus expelling the air. The turned-up end of the delivery-tube is then brought under the graduated-tube, and the part of the combustion-tube containing the carbonaceous residue heated gently. Then the part containing the pumice and mercuric sulphate is heated, and when it is red hot, that containing the residue is heated to strong red heat. When gas ceases to be evolved, heat the rest of the carbonate to sweep the tube. Transfer the receiving-tube to a water-trough, when the mercury and potash will be replaced by water. Measure the nitrogen, making corrections for temperature and pressure, and calculate nitrogen. (Fres., *Quant. Anal.*, § 249, 4th London Edition.)

To determine vanadium, dissolve 40 or 50 gms. of the iron, reduced to a finely-divided condition by filing or drilling, in dilute sulphuric acid. Filter out and wash the black residue, which will contain all but traces of the vanadium, and proceed as directed in *Appendix 3*, of "Complete Analysis of Iron Ore." (Consult, also, H. Rose, *Quant. Anal.*, p. 498.)

To determine molybdenum, treat a large quantity of the iron, as for vanadium, with dilute sulphuric acid. Filter out and wash the residue, digest it with yellow ammonium sulphide, which will dissolve the molybdenum, with other



metals whose sulphides are soluble in the alkaline sulphides. Filter, wash, and acidulate the filtrate. To re-precipitate the sulphide, filter, wash, digest with strong nitric acid to oxidize the sulphur, make alkaline with ammonia, and filter. All molybdic acid should go into solution. Then make the solution *slightly* acid with nitric acid, allow it to stand for some hours, and add solution of neutral mercurous nitrate in sufficient quantity. The yellow precipitate, which is at first bulky, soon contracts. Filter on a weighed filter, wash with a dilute solution of mercurous nitrate, dry, transfer the dry precipitate as completely as possible from the filter to a platinum or porcelain crucible, and ignite in a stream of hydrogen, cool, and weigh, and repeat until the weight remains constant. The heat should not be raised above gentle redness. Finally, weigh the dioxide, and calculate the molybdenum. As molybdic acid is volatile, instead of burning the filter, weigh it, and from the weight of the small portion of precipitate adhering, calculate the molybdenum, and add the weight to the other. (See H. Rose, *Quant. Anal.*, article "Molybdenum," p. 490.)

To determine any slag that may be mixed with cast-iron, pulverize about 3 gms. as finely as possible by boring with a dull drill and rubbing in a steel mortar, being careful not to lose any of the dust. Add this (little at a time) to 6 c. c. of bromine, previously mixed with 60 c. c. of water which has been boiled and cooled to 0° C. in a beaker of about 100 c. c. capacity. Keep the fluid at 0° C. for 3 hours, with frequent stirring. No evolution of gas should take place. After the iron appears to have dissolved, allow the fluid to stand for 24 hours at the ordinary temperature of the atmosphere. Then add 30 c. c. of ice-water, which has been previously boiled, allow the mixture to settle, and decant, on a small filter, the fluid containing light particles of carbon. Repeat, until only hard, dark powder remains at the bottom of the beaker. Test this for undissolved iron, by adding 2 drops of hydrochloric acid,

and 5 c. c. of water. If any iron be present, gas will be evolved. Whether iron be present or not, decant immediately on the filter, and wash, to avoid affecting the slag. If the hydrochloric acid has shown the presence of iron, add 30 c. c. of ice-cold water, which has been previously boiled, and 3 c. c. of bromine, and proceed as in the first instance, in order to dissolve all iron. Filter, and wash with cold water, until the washings give no reaction for iron. Dry the filter and contents, ignite, transfer the ignited substance to a silver or platinum dish, add solution of pure sodium hydrate, and digest, to dissolve free silica. Then filter, wash well, dry, ignite, cool, and weigh the slag. Iodine may be used instead of bromine. If iodine be used, add the same quantity of iron, reduced to as fine a powder as possible, to 15 gms. of iodine, covered with 15 c. c. of water, in a beaker of about 100 c. c. capacity, the water having been boiled previously to remove any air adhering to the iodine, and cooled by standing in ice. After adding the iron, proceed as when bromine is used.

Consult Fres., *Zeits. für Anal. Chem.*, 1865, pp. 69-77; Wag., *Jahresb.*, 1863, p. 19; same, 1865, p. 27; same, 1868, p. 28; *Comp. Rend.* 2, p. 1030; Dingler, *clxxvii.*, p. 388; Eggertz, *Jahresb.*, 1863, p. 30.

## CHAPTER XVIII.

### ZINC ORE.

Make a qualitative examination of the ore, for metals of Groups V. and VI.

Treat 2 gms. of the finely pulverized ore, in a small flask, with a mixture of 10 c. c. of hydrochloric acid, 5 c. c. of nitric acid, and 5 c. c. of sulphuric acid ; all the acids being pure and concentrated. Boil, until copious fumes of  $\text{SO}_3$  are evolved, cool, dilute with 25 c. c. of water, filter, and wash well. If the qualitative analysis has shown the presence of oxides of the higher groups, add 5 c. c. of hydrochloric acid, and saturate the solution, which should not exceed 500 c. c., with sulphuretted hydrogen. Filter, wash slightly, digest the precipitate with a mixture of 5 c. c. of hydrochloric acid, and 10 c. c. of water, over heat, dilute to about 400 c. c., and, without filtering, saturate with sulphuretted hydrogen. (See Fres., *Quant. Anal.*, § 162—A, p. 375.) Filter, wash well with hot water, combine the filtrates, and boil, after adding a little potassium chlorate to oxidize the sulphur, and precipitate basic acetates as usual. If no metals of the higher groups be present, the treatment with sulphuretted hydrogen and potassium chlorate is to be omitted. In either case, filter out the precipitate of basic acetates, dissolve it in hydrochloric acid, dilute, and precipitate again in the same way. Filter, dissolve the precipitate as before, and precipitate, a third time, with large excess of ammonia, filter, and wash. Combine all the filtrates, concentrate them to 500 c. c., acidify strongly with acetic acid, boil, and, while boiling, pass a rapid current of sulphuretted hydrogen for half an hour. By this means, the zinc will be precipitated as sulphide, and the manganese be held in solution. (See Fres., *Quant. Anal.*, § 160—6—a ; also

Gibbs, in *Am. Jour. Sci. and Arts*, January 7, 1868.) If there be a very large amount of manganese in the ore, it is well to dissolve the zinc sulphide in hydrochloric acid; make the solution slightly alkaline with sodium carbonate, and then decidedly acid with acetic acid, boil, and treat with sulphuretted hydrogen as before, as the zinc may carry down some manganese with it. Filter out the zinc sulphide, wash it by decantation 2 or 3 times with hot water, and then, on the filter, with sulphuretted hydrogen water, into small beakers, changing them often, in order not to be compelled to refilter a large amount of fluid, should the zinc sulphide run through the filter, which it is apt to do, as soon as the ammonium chloride is washed out. Ammonium chloride should be washed out, as it renders zinc carbonate soluble to a certain extent, when the solution is afterward treated with sodium carbonate. Should the zinc sulphide begin to run through the filter, stop washing, and, into the last turbid filtrate, wash the precipitate from the filter as completely as possible with water, dry the filter, moisten it with nitric acid, burn it, and add the ash to the precipitate. Then, add concentrated hydrochloric acid, and a little potassium chlorate, and boil until the zinc is dissolved, and the sulphur oxidized. After this, dilute to 300 c. c. for each 0.500 gms. of zinc oxide present and heat to boiling. Then, remove the heat, cover the vessel, add excess of sodium carbonate, and boil, to expel free carbonic acid. Wash three times by decantation with hot water, boiling up each time, and then on the filter thoroughly, and dry the precipitate. Brush the dry precipitate as completely as possible from the filter into a clock-glass, burn the filter in a weighed crucible, after moistening it with nitric acid, and carefully expelling the excess by heat, transfer the precipitate to the crucible, ignite again, cool, and weigh the impure zinc oxide. Should any zinc carbonate adhere to the vessel in which it was precipitated, dissolve it off into a weighed dish, evaporate to dryness, ignite, weigh,

and add the weight to that of the main precipitate. Dissolve the ignited precipitate in hydrochloric acid, filter out any undissolved silica, wash, ignite, weigh, and deduct its weight from that of the weighed precipitate. To the filtrate, add large excess of pure potassium hydrate, filter out any metallic oxides which have been precipitated by the potassium hydrate, dissolve them in hydrochloric acid, and repeat the treatment. Deduct their weight, also. The remainder will be zinc oxide, from which calculate metallic zinc.

As sodium carbonate sometimes fails to precipitate all the zinc, the filtrate from the zinc carbonate should be treated with sulphuretted hydrogen, and, if any zinc be recovered, its weight, after proceeding as before, should be added to the first.

A great many methods, principally volumetric, have been proposed with the view of saving time and labor, in the determination of zinc. Only one, that of Fahlberg, published in *Fres., Zeitsch.*, IV Hft. 1874, will be given here, with references to others.

For the determination of zinc in its ores, Fahlberg dissolves them with nitric and hydrochloric acids, adds an excess of the latter, and treats with a current of hydro-sulphuric acid to remove the metals of Groups V. and VI. After filtering, the iron is oxidized with nitric acid, and, when cold, precipitated with ammonium hydrate, the zinc remaining in solution. If the iron should be found to contain zinc, it must be dissolved in hydrochloric acid and re-precipitated. The two filtrates are then to be added to each other for titration. This ammoniacal solution is neutralized with hydrochloric acid, and further 10 to 15 c. c. acid (sp. gr. 1.12) is added, and the titration with the ferrocyanide solution can then be made. The normal solution of potassium ferrocyanide is usually prepared so that 1 c. c. corresponds to 0.01 gm. of zinc, and for this purpose it is first titrated with a solution of pure zinc. The metal is first dissolved in hydrochloric acid, and to

the solution ammonium chloride to the extent of five times the weight of the metal is added, so as to obtain the flakes of the precipitate as fine as possible, that they may not, while settling to the bottom, mechanically inclose the potassium ferrocyanide. In this way, about 0.5 gm. zinc is to be prepared, and the titration performed with a burette provided with a good glass stopper, and divided into .1 c. c. At first, large flakes are obtained, but as the operation proceeds, they constantly grow finer. After each addition of the ferrocyanide, a drop is to be taken from the beaker and tested with solution of uranic nitrate, to ascertain whether the whole of the zinc has been converted into ferrocyanide, and an excess of the normal solution added. For this purpose, a porcelain slab is used, which is previously moistened with a row of drops of the uranium solution. To these drops is added, in succession, after each addition of the normal solution, a drop of the solution in course of determination; toward the close, after every five drops of normal solution. As long as zinc remains in solution, only the white flakes of ferrocyanide of zinc are seen on the slab, but on the addition of only a very few drops in excess of the ferrocyanide a permanent brown spot is obtained. With careful manipulation the greatest possible error is 0.2—0.3 per cent, but even this could be diminished one half by the use of a normal solution of half strength. (See translation of Fahlberg's article, by Charles A. Schaeffer, Ph. D., in *Am. Chem.*, Vol. V., June, 1875.) It has been suggested that the accuracy of the method is increased by titrating the solution hot.

For other methods, consult Fres., *Quant. Anal.*, § 248, 4th London Edition; also Crookes's *Select Methods*, p. 61; also *Am. Chem.*, Vol. II., February, 1872.

## CHAPTER XIX.

### NICKEL ORE.

Make a qualitative examination for metals of Groups V. and VI.

Treat 5 gms. of the ore in a small flask with a mixture of 10 c. c. of sulphuric, 10 c. c. of nitric, and 5 c. c. of hydrochloric acids, all pure and concentrated, heating until copious fumes of sulphuric anhydride are evolved, adding more sulphuric acid if necessary, to avoid reducing the mass to dryness. Finally, cool the contents of the flask, dilute, filter, and wash thoroughly.

If the qualitative examination has indicated the presence of metals of the higher groups, dilute the solution of 5 gms. to 500 c. c., saturate with sulphuretted hydrogen, filter out any precipitated sulphides, and wash well. Add to the filtrate a little hydrochloric acid and potassium chlorate, and boil to oxidize sulphur and ferrous oxide.

If there be no metals of the higher groups present, of course the treatment with sulphuretted hydrogen, and after oxidation with potassium chlorate, is to be omitted. Dilute the filtrate, after boiling, with hydrochloric acid and potassium chlorate if sulphuretted hydrogen has been used, or the first filtrate, after decomposing the ore with acids, if no sulphuretted hydrogen has been used, to 1 litre, and add, with constant stirring, dilute ammonia until the solution is alkaline. Then filter out the precipitated ferric hydrate, and wash slightly. Dissolve the precipitate with dilute hydrochloric acid, and precipitate again with dilute ammonia. Filter, wash, combine the filtrates, concentrated to 500 c. c., acidify slightly with acetic acid, boil, and saturate with sulphuretted hydrogen, continuing the boiling while introducing the gas. Filter out, and wash the precipitated sulphides of nickel

K H C  
and cobalt, and wash them with sulphuretted hydrogen water. Should any manganese oxide be present, it will be held in solution. To recover any possible traces of nickel and cobalt, add a little more acetic acid to the filtrate, and boil. Should any sulphide be recovered by this treatment, wash it and the main precipitate from the filter into a casserole, dry and burn the filters, add the ash to the precipitates, and dissolve all with nitro-hydrochloric acid. Expel excess of acid by evaporating nearly to dryness, dilute, precipitate the oxides of nickel and cobalt by adding to the solution an excess of pure potassium hydrate, and heating for some time nearly to boiling, and separate the two metals by one of the following methods. (See Fres., *Quant. Anal.*, § 110—b— $\alpha$ , p. 188, and § 111.)

Hg C  
The first method is due partly to Liebig and partly to Wöhler. Wash the two oxides from the filter into a beaker, run through the filter, in order to dissolve what adheres, a saturated solution of pure potassium cyanide, into the beaker containing the oxides, and warm until they are dissolved. The solution looks reddish yellow. Heat to boiling to remove the free hydrocyanic acid. By this process the double cyanide of cobalt and potassium in the solution is converted, with evolution of hydrogen, into cobalticyanide of potassium, while the double cyanide of nickel and potassium in the solution remains unaltered. Add to the hot solution finely pulverized and elutriated mercuric oxide (red oxide), and boil. By this operation, the whole of the nickel is precipitated, partly as sesquioxide, partly as cyanide, the mercury combining with the liberated cyanogen. The precipitate is greenish at first, or, if the mercuric oxide has been added in excess, yellowish gray. Wash and ignite. The residue is oxide of nickel (NiO). (See Fres., *Quant. Anal.*, § 100-14—b.)

To determine the cobalt in the filtrate, Wöhler directs to carefully neutralize it with nitric acid, and add solution of mercurous nitrate, as long as it produces a precipitate of mercury cobalticyanide. The precipitate, after



washing and drying, is to be ignited with access of air, when it is weighed as black oxide of cobalt ( $\text{Co}_3\text{O}_4$ ). He suggests that, on account of its oxygen varying according to the temperature, it is better to reduce it by ignition in a strong current of hydrogen, and weigh the metallic cobalt. (See Wöhler's paper in *Annal. d. Chem. u. Pharm.*, LXX., 256, or his *Mineral Analysis*, p. 102. Care must be taken in neutralizing the filtrate before adding the mercurous nitrate, as the fluid must not be acid, and must not be strongly alkaline. The ignited oxide of nickel is very apt to contain some impurities; consequently, it is better to transfer it from the crucible to a beaker, boil it with water, throw it on a filter, wash, dry, ignite, weigh again, and subtract the loss, probably some adhering alkali. Then dissolve it in aqua regia, dilute, filter, wash, dry, ignite, and weigh any undissolved silica, and deduct its weight also. Finally, add to the filtrate a large excess of ammonia, filter out, wash, dry, ignite, and weigh any alumina and ferric oxide that may be present. After deducting their weight from that of the original precipitate, the remainder will be the true weight of the oxide of nickel. From this, calculate the metallic nickel.

Another method of separating the two metals is by means of potassium nitrite, recommended by H. Rose, and Fresenius as the best. (See Fres., *Quant. Anal.* § 160-9, p. 366). Dissolve the sulphides (obtained after precipitating the basic acetates, as directed before), in aqua regia, evaporate the solution nearly to dryness, and neutralize with potassium hydrate. Then add a concentrated solution of potassium nitrite (previously neutralized with acetic acid, and filtered from any flocks of silica and alumina that may have separated) in sufficient quantity, and finally acetic acid, till any flocculent precipitate that may have formed from excess of potassa has redissolved, and the fluid is decidedly acid. Allow it to stand at least for 24 hours in a warm place; take out a portion of the supernatant fluid with a pipette, mix it with more nitrite, and

observe whether a further precipitation takes place in this after long standing. If no precipitate is formed, the whole of the cobalt has fallen down; otherwise, the small portion must be returned to the principal solution, some more nitrate added, and, after long standing, the same test applied. Finally, filter and wash the precipitate thoroughly with an aqueous solution of neutral potassium acetate (containing 10 per cent of the salt), displace finally the last portion of solution of potassium acetate adhering to the precipitate, by means of alcohol of 80 per cent, and dry. Then transfer the precipitate from the filter to a clock-glass, incinerate the filter in a weighed crucible, add the precipitate, and gently ignite all. Cool, moisten with sulphuric acid, cautiously expel excess of acid, and ignite at low red heat. Cool and weigh the sulphate of cobalt and potassium ( $2\text{CoSO}_4 + 3\text{K}_2\text{SO}_4$ ), and calculate the cobalt. One hundred parts of the residue are equivalent to 18.015 parts  $\text{CoO}$ , or 14.17 parts  $\text{Co}$ . (See Fres., *Quant. Anal.*, § 81 or *Annal. d. Chem. u. Pharm.*, CIV., 309.)

To determine the nickel, mix the filtrate with pure solution of sodium or potassium hydrate in excess, heat for some time nearly to ebullition, decant 3 or 4 times, boiling up each time, filter, wash the precipitate thoroughly with hot water, dry, and ignite. After weighing the precipitate, treat it as directed in the first method, and deduct the weight of impurities. (Consult Fres., *Quant. Anal.*, § 110 p. 187.)

Another good method of determining the nickel, and cobalt in ores, is to decompose them in the same manner as directed above, remove any metals of Groups V. and VI. with sulphuretted hydrogen in acid solution, filter, oxidize the filtrate by boiling it with hydrochloric acid and potassium chlorate; dilute to about 1 litre. If no metals of the higher groups are present, the treatment with sulphuretted hydrogen, and potassium chlorate is to be omitted, and the original acid solution diluted to about 1 litre. Then make the solution alkaline by adding dilute

ammonia, and stirring constantly. Filter out any precipitate, dissolve it with hydrochloric acid, and precipitate again in the same way. Combine the filtrates, concentrate them to 100 c. c., add a little ammonia, transfer to a weighed platinum dish, and precipitate the nickel and cobalt together by passing a strong galvanic current, from a battery of 2 or 3 Bunsen elements, keeping the solution alkaline with ammonia. The nickel and cobalt will be precipitated upon the platinum in the form of a metallic coating. When the separation from the solution is complete, remove the dish, wash it thoroughly with hot water, dry and weigh it. The increase in weight expresses the combined weight of metallic nickel and cobalt. It remains to separate and determine them. Dissolve them with nitric acid; determine them by either of the preceding methods.

The following method of analysis of nickel and cobalt ores is from the pen of Fresenius, published in his *Zeit. für Anal. Chem.*, and translated by Prof. C. A. Schaeffer. (See *Am. Chem.*, IV., p. 289.)

The finely-powdered mineral or metallurgical product is treated with hydrochloric acid, with addition of nitric acid, until all soluble matter has been brought into solution, and repeatedly evaporated, with addition of hydrochloric acid, almost to dryness, in order to drive off the excess of nitric acid. Dilute hydrochloric acid and water are then added to the residue, after which it is filtered. If the insoluble portion is not perfectly white it is fused with acid potassium sulphate, the mass treated with hydrochloric acid and water, filtered, and the filtrate added to the original solution. The metals of Groups V. and VI. are next precipitated by hydrosulphuric acid. For this purpose, it is well to pass the gas through the solution at first at about 70° C., and afterward in the cold. The filtered solution is then warmed, and the iron oxidized with nitric acid; ammonia in excess is then added, and the impure ferric hydrate filtered off. After washing,

this is dissolved in hydrochloric acid, the solution largely diluted, and, after addition of ammonium chloride, a dilute solution of ammonium carbonate is added, in the cold, until a point is reached where the liquid becomes cloudy, but no precipitate is visible. On standing, the liquid should not again become clear, but rather more cloudy, although the reaction at this point must be definitely acid. It is next heated to boiling, the precipitate of basic oxide of iron is washed, first by decantation and afterward on the filter with boiling water; a portion of the precipitate is then examined for nickel by dissolving it in hydrochloric acid, repeating the precipitation as basic oxide, and testing the filtrate with ammonium sulphide, in order to see whether it is perfectly free from that metal. If, in this operation, a small amount of nickel should still be found, the whole precipitate must be dissolved in hydrochloric acid, and the iron again separated as basic oxide, as above. The two, or, as the case may be, three filtrates which contain nickel and cobalt are next acidulated with acetic acid, and concentrated by evaporation. If, by this means, a trifling precipitation of ferric or aluminic hydrate take place, the precipitate must be filtered off, dissolved in hydrochloric acid, and again separated with ammonia in excess, and this operation repeated once more. The filtered solution, containing all the nickel and cobalt, having been sufficiently concentrated, is treated with sodium carbonate until the reaction is decidedly alkaline, acetic acid is then added to acid reaction, and, to the clear liquid (30-50 c. c.), a solution of sodium acetate (1:10) is added. Hydrosulphuric acid is then passed through the solution, warmed to about 70° C., until the latter is saturated with that gas. The separation being completed, the precipitate of the sulphides of nickel and cobalt is filtered, washed, and dried. The filtrate is concentrated by evaporation; hydrosulphuric acid, ammonium sulphide, and acetic acid are added to it, and thus frequently a little more of the sulphides of nickel and

cobalt is obtained. It is well to test the filtrate in this way once again, in order to be quite sure that the whole of the nickel and cobalt has been obtained as sulphides. The dried sulphides of nickel and cobalt, together with the filter ash, are now treated with hydrochloric acid, with addition of nitric acid, until all has been dissolved, the solution evaporated with addition of hydrochloric acid in order to drive off the nitric acid, diluted with water, filtered, and the nickel and cobalt precipitated with pure potassium hydrate in a large platinum dish. The precipitate obtained must be very thoroughly washed by decantation afterward on the filter, with boiling water, dried, incinerated and heated to bright redness in a Rose crucible, in a current of pure hydrogen, until the weight remains constant. The metallic nickel and cobalt are next treated in the crucible with boiling water. Should this show an alkaline reaction or the presence of chlorine or sulphuric acid, or yield a residue when evaporated on platinum foil, the metals must be exhausted with boiling water, heated in a current of hydrogen, and again weighed. The metals are now dissolved in hydrochloric acid, after which a small amount of silicic acid usually remains. This is to be collected on a filter, burned, and weighed. The hydrochloric acid solution is nearly neutralized with ammonia; ammonium carbonate is added in excess, and the liquid slightly warmed for some time. A trifling precipitate of ferric and aluminic hydrates, which in most cases is obtained, is filtered, dissolved in hydrochloric acid, again precipitated, and ignited, first in the air and then in a current of hydrogen. Its weight, together with that of the silicic acid, is then to be subtracted from the original weight of the metals. As can easily be seen, it will in most cases be allowable, and a great saving of time, to incinerate the little filter containing the silicic acid, and that containing the ferric and aluminic hydrates in the same small crucible, and then, after treatment with hydrogen, to weigh all these impurities together. Should,

however, the ash of these, in consequence of the presence of a small amount of cobalt, appear bluish, it must be fused with an alkaline carbonate, and the silicic acid, etc., thus obtained be perfectly pure.

If the ore or metallurgical product contain zinc, the nickel and cobalt obtained by the above method would be contaminated with that metal, since zinc cannot be entirely removed either by the precipitation of the hydrates with excess of potassium hydrate, or by the reduction of the oxides in a current of hydrogen. In this case, the hydrochloric acid solution of the metals precipitated by ammonium sulphide is evaporated to a small volume; and pure, finely-crystallized ammonium chloride is added to it in such quantity that, for 0.2 gm. oxide of zinc, there shall be about 5 gms. ammonium chloride. It is then evaporated to dryness on a water-bath, and carefully heated, until all the ammonium chloride, and with it all the zinc, is driven off. The residue, which consists of metallic nickel and cobalt, is dissolved in hydrochloric acid, with the addition of nitric acid, the greater part of the excess of free acid driven off, and the oxides precipitated with potassium hydrate, and further treated exactly according to the above method.

If nickel and cobalt are to be determined separately, the ammoniacal filtrates, obtained after separation of the contaminating substances, are evaporated to dryness, the ammonium compounds are driven off by gentle heat, the residue dissolved in hydrochloric acid, with addition of nitric acid, and if much nickel and little cobalt are present, the latter is separated by means of potassium nitrite. If, on the contrary, much cobalt and little nickel are present, it is found more advisable to add, to the solution of the chlorides, potassium cyanide in excess, and to precipitate the nickel as the black hydrate oxide of nickel, by warming with bromide after the addition of the potassium hydrate. In the first case, the potassio-cobaltic nitrite, and in the second, the hydrated oxide of nickel, is dis-

solved in hydrochloric acid, precipitated with potassium hydrate, and determined in the metallic condition. In these determinations, the weighings must be followed by an examination for silicic acid, and impurities insoluble in ammonium carbonate.

NOTE.—For the determination of nickel and cobalt by the battery see Luckow, Fres., *Zeitschrift für Anal. Chem.*, XIX., p. 1., or Dingler's *Polyt.*, vols. CLXXVII and CLXVIII. Organic salts, as acetates, etc., aid this precipitation (Luckow). Ammonium chloride in the solution interferes with this separation according to Luckow (Fres., *Zeitschrift*, XI., 11), Wrightson (*ibid.*, XV., 297), Schroeder (*ibid.*, XVI., 344), Beilstein (*Berichte Deut. Chem. Gesell.*, XI., 1715), Riche (*Comptes Rend.*, LXXXV., 226) and others.

## CHAPTER XX.

### COPPER ORE.

For directions for making a complete analysis of copper ore, consult Fres., *Quant. Anal.*, § 242. It is proposed here to give directions for the separation and determination of copper alone.

The first step is to make a careful qualitative examination of the ore. Then introduce 1 gm. of finely-pulverized ore into a flask holding about 200 c. c., add 5 c. c. nitric, 2 c. c. hydrochloric, and 10 c. c. sulphuric acid (the acids should all be pure and concentrated), boil until all the nitric acid is expelled, and dense white fumes of  $\text{SO}_3$  are evolved. The flask should be filled with them. Then cool, dilute with about 50 c. c. of water, filter, and wash with about 75 c. c. more. Digest the residue with nitric and hydrochloric acids, and if the solution gives any reaction for copper, add sulphuric acid and treat as before. Treat a third time, if necessary.

If the ore be very poor, more than 1 gm. should be taken, and treated with a corresponding amount of the three acids.

Should no metals of Group VI. or any of Group V. besides copper be present, dilute the solution to 200 c. c., or if it already exceeds that volume, concentrate to 200 c. c., and divide into two exactly even parts. Introduce each into a weighed platinum dish, and precipitate the copper by a galvanic current, the dishes being connected with the zinc or negative pole of a battery (consisting of at least two Bunsen elements) by resting on a coil of the wire or a copper disk to which the wire is soldered, while the fluid in the dishes is connected with the positive pole by a wire attached to platinum foils which hang in the fluid. When the copper is entirely precipitated (which can be determined by testing a few drops of the



fluid with sulphuretted hydrogen water), pour out the contents of the dishes into a beaker, wash them (two or three times) with hot water into the same beaker, and then with alcohol, to displace the water, decanting the alcohol off, as completely as possible, into another vessel. Then dry the dishes over a low flame until the small quantity of alcohol adhering to the copper is expelled, and weigh them. The increase in weight represents the weight of metallic copper. The difference in weight of copper in the two dishes should not exceed one tenth of one per cent. Should it do so, another determination must be made.

In evaporating off the alcohol, the dishes should not be allowed to become so hot that they cannot be carried to the balance on the naked hand, and be cool enough to weigh in five minutes. It is unnecessary to place them in a desiccator.

The copper should be bright red in color, free from all dark spots, and so firmly attached to the dish as not to be washed off by water. The formation of spongy copper is an indication that too much ore has been used for the capacity of the dish, or that the current has been too intense.

This is the best method in most cases.

To prove the accuracy of this method, Mohr mixed 1 gm. of pure metallic copper with 0.5 gm. of gold, silver, platinum, tin, lead, iron, zinc, nickel, cobalt, bismuth arsenic, uranium, mercury, molybdenum, antimony, sulphur, silica, and calcium phosphate, treated the mixture in a similar manner, precipitating the copper in a platinum dish with metallic zinc instead of the galvanic current, and recovered 0.996 gm. of copper. In more than 20 determinations of copper in various combinations, the average amount of the metal obtained by this method was 99.7 per cent of the actual quantity present.

If arsenic or antimony be present in the ore, it is safer to remove them by saturating the solution with sulphuretted hydrogen, making it alkaline with potassium

hydrate, and warming gently for some time to dissolve the sulphides of arsenic and antimony. Filter and wash the copper sulphide, which may contain some other sulphides of metals of Group V. If it does not contain them, or only lead sulphide, dissolve in nitric acid, add sulphuric acid, evaporate to dense fumes of  $\text{SO}_3$ , cool, dilute, filter out any insoluble residue, and proceed to determine the copper electrolytically, as directed above. When other metals of Group V. are present, treat the sulphides with pure potassium cyanide, which will dissolve the copper sulphide, and leave the others undissolved. Then treat the solution with nitric acid, boil to expel hydrocyanic acid, add sulphuric acid, heat to expel nitric acid, and proceed as before.

*Determination as cuprous sulphide ( $\text{Cu}_2\text{S}$ ):*

Instead of dissolving the copper sulphide in nitric acid, and evaporating the solution after addition of sulphuric acid, dry it, transfer the precipitate to a watch-glass, burn the filter in a weighed porcelain crucible provided with a perforated cover (known as Rose's crucible), add the precipitate and some pure powdered sulphur, and burn in a current of hydrogen, over a blast-lamp. Weigh as  $\text{Cu}^2\text{S}$ . (Compare H. Rose's *Quant. Anal.*, pp. 105 and 255, chapter on copper; also, Fres., *Quant. Anal.*, § 119-3, p. 230, and *Jour. f. Prakt. Chem.*, CVII., 110, and LXII., 252. The results are very accurate. The method is the best one, where the electrolytic method cannot be conveniently applied.

*Determination as oxide:*

Decompose the ore as directed in the first instance, and, after separating the copper from other associated metals, as directed above, add to the solution, after evaporating off excess of acid, and heating to boiling, dilute solution of pure potassium or sodium hydrate, in excess, and continue to boil until the cupric hydrate, which is pale blue, is converted into brownish black cupric oxide. Allow the precipitate to settle, filter, wash by decantation with boil-

ing water several times, transfer to the filter, wash well with boiling water, dry, ignite intensely, and weigh. Then add a few drops of nitric acid, evaporate off excess of acid, ignite cautiously, cool, and weigh. From the weighed cupric oxide calculate metallic copper.

The action of reducing gases must be carefully avoided. The addition of nitric acid, and second ignition is to overcome any difficulty arising from this cause. Consult Fres., *Quant. Anal.*, § 119—1—a., for precautions to be observed and difficulties to be encountered.

There are various volumetric methods of determining copper, for some of which consult Fres., *Quant. Anal.*, § 119, p. 225.

## CHAPTER XXI.

### GERMAN SILVER.

The metals to be looked for usually are copper, nickel, zinc, and iron, which last is sometimes added to make the metal white. Lead is sometimes found in small quantity.

Introduce 0.500 gm. of the alloy into a 200 c. c. flask, add 5 c. c. of concentrated nitric acid, and 15 c. c. of water, and heat until the alloy is dissolved. Then cool, add 10 c. c. of concentrated sulphuric acid, and heat until dense fumes of  $\text{SO}_3$  are evolved. Cool, dilute to 50 c. c., and filter out lead sulphate, if necessary. Divide the filtrate into 2 equal parts, and determine the copper in each electrolytically, as directed in the analysis of copper ore. Combine the solutions (after precipitating the copper) together with the washings (after boiling out the alcohol from them), add sodium carbonate until the fluid is slightly alkaline, and then acetic acid until it is acid, and precipitate basic ferric acetate as usual. Dissolve the precipitate in hydrochloric acid, re-precipitate the ferric hydrate by ammoniac hydrate, filter, dry, ignite, and weigh, and calculate it to metallic iron.

To the filtrate, add pure potassium hydrate in large excess. Nearly all the zinc will be held in solution, while the nickel, with, perhaps, a little zinc, will be precipitated. Allow the precipitate to settle, decant the clear fluid into another vessel, and add to the precipitate a concentrated and filtered solution of pure potassium cyanide, and digest over heat, until the precipitate goes into solution. It sometimes happens that a portion of it resists the action of the cyanide. When such is the case, filter it out, and as it contains no zinc, dissolve it in hydrochloric acid and potassium chlorate, and reserve it to be added to the solu-

tion containing the nickel after precipitating the zinc. Combine the other solutions containing zinc and nickel, neutralize with hydrochloric acid, leaving the fluid only slightly alkaline, add potassium sulphide until all the zinc is precipitated, filter, and determine the zinc as directed in analysis of zinc ore.

Add to the filtrate from the zinc sulphide, the solution of the small portion which resisted the action of potassium cyanide, add more hydrochloric acid, if necessary, and boil, to decompose the cyanides, and expel cyanogen. Then make the solution strongly alkaline with ammonia, filter out any ferric hydrate, calculate it to metallic iron, and add the per cent to that obtained from the acetate. In the ammoniacal filtrate from the ferric hydrate, determine the nickel electrolytically, as in the analysis of nickel ore.

As the above operations may introduce such amounts of salts as to interfere with concentration for the battery precipitation, it may be preferable to precipitate out the nickel and redissolve. In such a case add ammonium sulphide—stir it in well—render just acid with acetic acid, and allow the solution to stand for some time. Then decant through a filter, allowing as little of the precipitate as possible to get upon the filter; dissolve the precipitate in hot nitric acid, destroy the carbon of the filter by fusing with a small amount of alkaline nitrate, and add to the solution of the precipitate. The neutralization by ammonia, etc., may then be conducted as usual.

If the analysis be made entirely without the use of a battery, after dissolving the alloy, and removing any lead as above, precipitate the copper as sulphide, ignite it, after adding sulphur, in a current of hydrogen, and weigh the ignited precipitate as cupreous sulphide. (See analysis of copper ore.)

Boil the filtrate from the copper sulphide, with potassium chlorate, and determine the zinc, nickel, and iron as above.

## CHAPTER XXII.

### GALENA.

Treat 1 gm. with fuming nitric acid, and sulphuric acid.  
*Note 1.*

<i>Residue (a).</i>		<i>Filtrate (a).</i>	
Lead sulphate and gangue. <i>Note 2.</i>		Silver and other metals. <i>Note 4.</i>	
<i>Residue (b).</i>	<i>Solution (b).</i>	<i>Filtrate (e).</i>	<i>Precipitate (e).</i>
Lead carbonate and gangue. <i>Note 2.</i>	Alkaline sulphate reserve. Treat with $H_2S$ . <i>Note 2.</i>	Iron, zinc, copper, etc. <i>Note 4.</i>	Silver. <i>Note 4.</i>
<i>Solution (c).</i>		<i>Residue (c).</i>	
Lead acetate. <i>Note 3.</i>		Insoluble gangue. <i>Note 2.</i>	
<i>Precipitate (d).</i>		<i>Filtrate (d).</i>	
Lead sulphide. <i>Note 3.</i>		To be combined with <i>solution (b)</i> , <i>residue (c)</i> , and <i>filtrate (e)</i> . <i>Notes 3 and 4.</i>	

*Note 1.*—Introduce into a flask holding about 200 c. c., 1 gm. of finely pulverized galena, previously dried at  $100^{\circ}C.$ , add 4 or 5 c. c. of red fuming nitric acid, and cover with a watch-glass. After the violent action is over, heat on a water-bath for some time, to oxidize the sulphur. After the sulphur is oxidized, add 3 or 4 c. c. of sulphuric acid previously diluted with 3 or 4 c. c. of water, and heat over a burner until the nitric acid is expelled, and dense white fumes of  $SO_3$  appear. Then cool, dilute cautiously with about 50 c. c. of water, filter, and wash the residue containing lead sulphate and gangue, with about 100 c. c. of water containing 1 per cent of sulphuric acid, and then with 30 or 40 c. c. of alcohol.

There will be a *residue (a)* on the filter containing lead sulphate and gangue, and a *filtrate (a)*, containing silver, and other metals.

*Note 2.*—Wash *residue (a)* into a beaker, add about 50 c. c. of strong solution of ammonium carbonate, and digest

on a water-bath, with frequent stirring for 10 or 12 hours, to convert the lead sulphate into carbonate. Filter, and wash well with a solution of ammonium carbonate, and then with hot water to dissolve out all alkaline sulphate.

There will be a *residue* (*b*) of lead carbonate and gangue, and a *filtrate* (*b*) of alkaline sulphate. Dissolve the lead carbonate through the filter with hot acetic acid, keeping it covered until effervescence ceases, and is not renewed upon the further addition of acetic acid. Wash thoroughly, to remove all lead acetate from the gangue remaining on the filter. Treat *filtrate* (*b*) with  $H_2S$ , and add precipitate to *precipitate* (*d*).

There will be a *solution* (*c*) of lead acetate and a *residue* (*c*) of insoluble siliceous gangue.

*Note 3.*—Saturate *solution* (*c*) with sulphuretted hydrogen, filter, and wash with hot water. There will be a *precipitate* (*d*) of lead sulphide, and a *filtrate* (*d*) which is to be combined with *solution* (*b*), *residue* (*c*), and *filtrate* (*e*). Wash the lead sulphide, or *precipitate* (*d*), into a casserole, dry the filter, burn it in a porcelain crucible, after moistening it with a few drops of nitric acid, treat the ash with a little dilute nitric acid, and, when it is dissolved, wash the solution into the same casserole, add 3 or 4 c. c. of sulphuric acid, and heat until fumes of  $SO_3$  appear. Then cool, dilute with 30 or 40 c. c. of water, filter, wash with about 50 c. c. of water containing 1 per cent of sulphuric acid, and finally with about the same quantity of alcohol. Dry the filter and contents at a moderate heat (not over  $100^\circ C.$ ), and, when dry, brush the contents into a glass as completely as possible, burn the filter in the way directed above, in a weighed porcelain crucible, add to the ash 5 or 6 drops of nitric acid and 2 or 3 drops of sulphuric acid, evaporate the excess of acid, add the precipitate, and ignite all. Cool and weigh the lead sulphate, and calculate the lead.

*Note 4.*—To *filtrate* (*a*), containing the silver, add, after boiling out the alcohol, about 1 c. c. of hydrochloric acid.

Should any turbidity of the fluid be occasioned by the hydrochloric acid, let the solution stand for some hours in a warm place, until the precipitate settles, filter, and wash.

There will be a *precipitate* (e) of silver chloride, and a *filtrate* (e), containing other metals.

Dry the precipitate, remove it, if possible, from the filter, burn the latter in a weighed porcelain crucible, add to the ash a few drops of nitric acid and hydrochloric acid, evaporate to dryness, add the precipitate, and fuse at a low red heat. (See analysis of barium chloride.) From the weight of silver chloride, calculate the silver.

To *filtrate* (e), after adding *solution* (b), *residue* (c), and *filtrate* (d), add excess of sodium carbonate, and a little sodium nitrate, evaporate to dryness in a platinum dish, fuse, and determine the other constituents of the ore.

*Note 5.*—It is better to determine the sulphur in a separate portion. For this purpose, heat 1 gm. of the finely pulverized galena in a large porcelain crucible, at 100° C., with a strong solution of potassium hydrate, for an hour, and pass a slow current of chlorine through the fluid. The sulphur will be converted into sulphuric acid. Then filter, wash, acidify the filtrate with hydrochloric acid, and precipitate the sulphur as barium sulphate, as usual. Bromine may be used to oxidize the sulphur, instead of chlorine. (See *Jour. f. Prakt. Chem.*, LXI., 134, and *Compt. Rend.*, 37, 835.)

*Note 6.*—If it be desired to determine a small quantity of silver in the presence of a large quantity of lead, by a wet method, consult Fresenius's *Analysis of Refined Lead*, in *Zeits. für Anal. Chem.*, Vol. VIII., 1869.

**NOTE.**—The ammonium carbonate used in Note 2 should be a solution of the solid salt made *without* addition of ammonium hydrate. A more rapid method consists in using a solution of ammonium citrate with ammonia, which will at once dissolve the lead sulphate. From this solution, neutralized by sulphuric acid, the lead may be precipitated by H<sub>2</sub>S, and the precipitate converted into sulphate by oxidation with nitric acid, and subsequent treatment with sulphuric acid.



## CHAPTER XXIII.

### TIN ORE.

There are many methods proposed for the determination of tin in ores. Probably, the fusion of the ore with sulphur and sodium carbonate is, as Rose remarks, p. 392, the best. It requires, however, the exercise of great care and judgment to make it successful. It is as follows :

Fuse 1 gm. of rich ore, very finely pulverized, with 3 parts of sulphur, and 3 parts of dry sodium carbonate (after mixing the ore and flux thoroughly), in a large porcelain crucible, for about one hour, over a Bunsen burner. The heat should not be too great, or continued too long, as, under such circumstances, the sulphide of tin may be oxidized and become insoluble when the fused mass is treated with water. By the fusion, sulphides of tin and sodium are produced, and, upon adding water, the tin sulphide should go into solution in the sodium sulphide, as sodium sulpho-stannate, and will—if the fusion has been properly conducted. After fusing as directed, cool, place the crucible in a casserole, add hot water, and digest on a water-bath until the fused mass is disintegrated and removed from the crucible. Then filter, wash thoroughly with hot water, and acidulate with sulphuric acid, to precipitate the tin sulphide. Allow the sulphide to settle completely, in a warm place, pour the clear fluid on a filter, wash 4 or 5 times by decantation, and then moderately on the filter with hot water. Should the precipitate show an inclination to run through the filter, wash with solution of ammonium acetate (Bunsen). Put the filter, with the not yet quite dry precipitate on it, into a weighed porcelain crucible, and apply a very gentle heat, with free access of air, until the odor of sulphurous acid is no longer perceptible. Increase the heat now gradually, to

a high degree of intensity, and treat the residue repeatedly with some carbonate of ammonia, in order to insure the complete expulsion of the sulphuric acid which may be present. Were you to apply a very intense heat from the beginning, fumes of stannic sulphide would escape, which burn to binoxide (H. Rose, p. 393). The residue left after the first fusion and solution, should be fused again, and treated in the same way; and even a third and fourth time, or until no more tin can be recovered.

After weighing the stannic oxide, it should be examined for silica. To do this, weigh out a portion, and fuse it with 3 or 4 parts of a mixture of equal weights of sodium and potassium carbonates, boil with water, filter, wash, acidulate the filtrate with hydrochloric acid, and should silica separate, filter, and reserve the filter and contents. Then precipitate the tin with sulphuretted hydrogen, filter out the sulphide, and treat the filtrate as usual for silica, finally filtering through the reserved filter, already containing some silica. Calculate the silica thus found, to the whole amount of stannic oxide, and, after deducting it, calculate the metallic tin.

Examine the residue left (after fusing, and filtering out the solution of alkaline stannate as directed above) for iron, by dissolving it in hydrochloric acid and a few drops of nitric acid, and precipitating the ferric hydrate with excess of ammonia. Should any be found, it must be calculated to the whole amount of stannic oxide first weighed, and deducted from it, as was the silica. It must be calculated also to metallic iron, and the per cent added to that found elsewhere.

## CHAPTER XXIV.

### BRONZE.

The metals to be looked for are copper, tin, lead, zinc, and iron.

Dissolve 1 gm. of the alloy, in a small covered beaker, in a mixture of 2 c. c. of nitric acid, 8 c. c. of hydrochloric acid, and 10 c. c. of water, dilute to 200 c. c., heat gently, add crystals of sodium carbonate until a distinct precipitate forms, and boil until the basic carbonate of copper turns black. Then cool, add nitric acid, drop by drop, until the reaction is distinctly acid, and digest for several hours at a gentle heat until the stannic oxide is white. Then filter it out, wash, dry, ignite strongly, and weigh it. The stannic oxide must then be examined for silica and iron (as directed in the analysis of tin ore), which are to be deducted before calculating the tin. (See Fres., *Quant. Anal.*, § 164—B—4—a, p. 891.)

The ignited stannic oxide may be purified, by first treating it with sulphuric acid and ammonium fluoride (the silica being determined by loss), and then fusing it with the two carbonates, as in analysis of tin ore, dissolving and filtering out the stannate, and in the residue determining the ferric oxide, to be deducted from the stannic oxide, and also calculated to metallic iron, the per cent of which is to be added to that found elsewhere.

Evaporate the filtrate from the stannic oxide, after adding about 10 c. c. of sulphuric acid, until fumes of  $\text{SO}_2$  are evolved, dilute, filter out lead sulphate, and calculate lead. (See analysis of galena.)

After filtering out the lead sulphate, and washing, determine the copper in the filtrate electrolytically. (See analysis of copper ore.)

In the residual fluid, after extracting the copper, precip-

itate the zinc by sodium carbonate, and proceed as directed in the analysis of zinc ore. Dissolve the weighed zinc oxide in hydrochloric acid, filter out and determine any residual silica, and deduct its weight from that of the oxide. Then add to the filtrate, excess of pure potassium hydrate; filter out and wash the ferric hydrate, dissolve it in hydrochloric acid, and precipitate again with potassium hydrate, filter, wash, dry, ignite, and weigh the ferric oxide, which is also to be deducted from the first weight of zinc oxide. The remainder, after deducting the weight of silica, and that of ferric oxide, is to be calculated to zinc.

Combine the weight of ferric oxide found here, with that found in the purification of the stannic oxide, and calculate to metallic iron.

The analysis may be made in another way. Determine the tin and lead, as above, in the filtrate, precipitate the copper as sulphide, and determine it as cupreous sulphide. (See analysis of copper ore.) Then oxidize the sulphur in the solution, by boiling with potassium chlorate, and determine the zinc and iron as above.

## CHAPTER XXV.

### ARSENIC ORE.

Introduce 1 gm. of the finely pulverized ore, into a large, covered porcelain crucible, add 15 c. c. of strong nitric acid, and evaporate to pasty condition; then add 3 or 4 gms. of dry sodium carbonate, and as much sodium nitrate; heat cautiously to perfect dryness, and fuse until the contents of the crucible are fluid. Then cool, place the crucible and contents in a casserole, containing about 200 c. c. of water, and heat until the mass is disintegrated so far as to leave the crucible. Then remove the crucible, wash it, adding the washings to the fluid in the casserole, boil until the mass in the casserole becomes pulverulent, and the fluid concentrated to 150 c. c. Cool, add 50 c. c. of alcohol stir well, filter, wash with 40 or 50 c. c. of dilute alcohol, (containing 1 volume of alcohol, and 2 volumes of water). It is advisable to dry the residue, and repeat the fusion and other treatment, described above. Combine the solutions which will contain the arsenic, in the form of sodium arsenate, and also, perhaps, a little silica and alumina. Boil out the alcohol, keeping up the volume of fluid by occasionally adding water, and, after removing the alcohol, acidulate with nitric acid; add 50 c. c. of the ordinary solution of ammonium molybdate, and warm for several hours, to precipitate the arsenio-molybdate. After the precipitate has entirely settled, filter, and wash with the precipitant; dilute with an equal volume of water, as in the determination of phosphoric acid. Dissolve the precipitate through the filter with dilute ammonia, wash the filter well with the same, and allow the solution to stand 12 hours, when any silico-molybdate present will be decomposed, and the silica separate. Filter out the silica, wash with water, and acidify the filtrate with nitric acid.

The arsenio-molybdate will be precipitated, and the alumina remain in solution. Filter, wash with 30 or 40 c. c. of diluted ammonium molybdate solution, dissolve through the filter with ammonia diluted with an equal volume of water, wash with the same, and, to the filtrate, add 4 or 5 c. c. of "magnesium mixture," and allow it to stand for 12 hours. After the precipitate has settled, test as to whether or not a sufficient amount of the precipitant has been used, by mixing a few drops of the clear fluid with a little sodium phosphate. If no precipitate appear, which is very improbable, add more "magnesium mixture," and allow the whole to stand until the magnesium arsenate has had time to form and settle completely; then filter, and wash with dilute ammonia, containing one third its volume of alcohol. Dissolve the precipitate through the filter into a small beaker with dilute hydrochloric acid, add slight excess of ammonia, and alcohol to the amount of one third the volume of the solution, and allow all to stand for several hours. Then filter, wash with dilute ammonia containing alcohol, dissolve the moist precipitate through the filter with dilute nitric acid, into a small porcelain dish, or large porcelain crucible, previously weighed; evaporate to dryness, ignite gently at first, and then strongly, over a good Bunsen burner, and weigh the magnesium pyro-arsenate. (See *Jour. London Chem. Soc.*, August, 1877, p. 222; taken from *Zeit. f. Anal. Chem.*, XIV., 356.) The results are accurate. By the ordinary method of drying the precipitate of magnesium arsenate, on a weighed filter at 100° or 105° C., not only water is expelled, but also ammonia. (See a paper by MacIvor, in *Chem. News*, Dec. 17, 1875.) The author's experience confirms MacIvor's conclusion.

After weighing the magnesium pyro-arsenate, in order to test it for phosphoric acid, dissolve it in hydrochloric acid, add sodium sulphite, saturate with sulphuretted hydrogen, filter out the arsenious sulphide, wash well, add to the filtrate large excess of nitric acid, boil down to small

volume (repeating the addition of nitric acid and boiling, if necessary), until the sulphur is all oxidized, and hydrochloric acid expelled. Then add 10 or 15 c. c. of ammonium molybdate solution. Should a precipitate of phospho-molybdate occur, determine the corresponding magnesium pyro-phosphate, and deduct it from the magnesium pyro-arsenate weighed before, and calculate the arsenic.

Where absolute accuracy is not required, the analysis may be made more expeditiously by treating the ore with strong nitric acid, adding sodium carbonate and sodium nitrate, evaporating, and fusing in a platinum crucible, removing the heat as soon as the flux is fluid, and then digesting with hot water until the mass is pulverulent. By this means, the arsenic is dissolved as sodium arsenate, and can be filtered nearly pure. "Magnesium mixture" is now to be added to the solution directly, and the analysis conducted as above.

To insure the purity of the precipitate, it is well to dissolve it in nitric acid, filter out any insoluble residue, which is to be deducted, and also to test for phosphoric acid, which, if found, is also to be deducted.

NOTE.—Where the percentage of arsenic in the ore will probably amount to 20 or 25 per cent., it is usually advisable when the molybdate separation is used, to make the solution from 1 gm. up to some convenient bulk, and to take some fraction, as one-half or one-quarter, for the determination.

## CHAPTER XXVI.

### ANTIMONY ORE.

To determine the antimony, add, to 1 gm. of the finely pulverized ore, 5 c. c. of concentrated nitric acid, 10 c. c. of concentrated hydrochloric acid, 3 gms. of tartaric acid, and heat on a water-bath until the substance is nearly dry, in order to expel most of the free acid. Then dilute with 100 c. c. of water, make alkaline with ammonia, add 8 or 10 c. c. of yellow ammonium sulphide, and warm gently for an hour. Enough of the alkaline sulphide should be added to make the fluid yellow. Filter and wash with hot water until the washings run through the filter perfectly colorless. The filtrate will contain the antimony as ammonium sulph-antimonate. Acidulate the filtrate with hydrochloric acid, and allow the precipitate of antimony sulphide to settle completely. Dry the residue remaining upon the filter, fuse it with 4 or 5 gms. of sodium carbonate, and 1 gm. of sodium nitrate, treat the fused mass with an excess of hydrochloric acid and about 1 gm. of tartaric acid, evaporate off excess of acid as above, add 25 c. c. of water, make alkaline with ammonia, treat with yellow ammonium sulphide, filter, wash, acidulate the filtrate with hydrochloric acid, and, should any antimony sulphide be precipitated, allow it to settle as directed before. Filter out the precipitates of antimony sulphide on the same filter, wash with hot water, then with alcohol to displace the water adhering to the precipitate, dry it at a low heat, wash with carbon disulphide, to dissolve the free sulphur, and dry at a temperature not over 100° C. The heat should be moderate, and continued no longer than is necessary. When the precipitate is dry enough to be removed from the filter, brush it into a clock-glass, cleaning the paper as thoroughly as pos-



sible, and place the filter in a capacious weighed porcelain crucible, furnished with a cover. Moisten it with ordinary concentrated nitric acid, add 4 or 5 c. c. of red fuming nitric acid, and evaporate on a water-bath to dryness. Then transfer the precipitate to the crucible, add a little concentrated nitric acid cautiously by means of a pipette, inserting the point of the pipette under the edge of the lid. When the violent action is over, add also to the precipitate 8 or 10 times its volume of red fuming nitric acid, observing the same precautions as before, and evaporate to dryness on a water-bath, having removed the cover from the crucible as soon as all danger of loss by spiriting is past. Finally, ignite cautiously over a Bunsen burner, to expel the sulphuric acid, and convert the precipitate into antimony tetroxide ( $\text{Sb}_2\text{O}_4$ ), from which calculate the antimony. This method is due to Bunsen. (See Fres., *Quant. Anal.*, § 125, 2, b, p. 243.) All the filtrates should be treated again with sulphuretted hydrogen, to recover any possible traces of antimony which may have escaped precipitation before.

## CHAPTER XXVII.

### TYPE METAL.

The metals to be looked for are antimony, lead, tin, and iron. In rare cases, a little arsenic may be present.

To 1 gm. of the metal, comminuted, by drilling, shaving, or filing, add 3 or 4 gms. of tartaric acid, and 20 c. c. of dilute nitric acid, prepared by mixing 1 part of concentrated nitric acid with 2 parts of water. Digest on a water-bath until excess of nitric acid is entirely expelled, add 50 c. c. of water, excess of ammonia, 10 c. c. of yellow ammonium sulphide, and allow to stand on a water-bath for 3 or 4 hours, the water in the bath being heated to a point just below boiling. Do not heat strongly. Dilute to about 100 c. c., filter, and wash with water until the washings are colorless. The oxides of antimony and tin go into solution as ammonium sulphantimonate and sulpho-stannate, while the lead and iron sulphides remain on the filter undissolved. Wash the contents of the filter, dry the filter, burn it in a porcelain crucible, after moistening with nitric acid, add to the ash 5 or 6 drops of nitric acid, warm, and wash it into the casserole. Then add 6 or 7 c. c. of nitric acid and 2 or 3 c. c. of sulphuric acid, and heat until fumes of  $\text{SO}_3$  appear; cool, add 50 c. c. of water, filter, and wash with 40 or 50 c. c. of water containing 1 per cent of sulphuric acid. Dry the filter and contents, transfer the latter to a clock-glass, place the filter in a capacious weighed porcelain crucible, add 8 or 10 drops of nitric acid and 4 or 5 drops of sulphuric acid, evaporate off the excess of acid, and ignite. Again add 4 or 5 drops of nitric acid and 1 or 2 drops of sulphuric acid, expel excess of acid, transfer the contents of the filter from the clock-glass to the crucible, ignite all,

cool, weigh the lead sulphate, and calculate the per cent of lead. (Consult analysis of galena.)

Acidify the alkaline filtrate containing the tin and antimony, and perhaps some arsenic, with hydrochloric acid, and allow the sulphides to settle in a warm place, avoiding great heat. Then filter, wash with water, displace the water with a little alcohol, dry at a moderate heat, run a little carbon disulphide through the filter, to dissolve out free sulphur, expel excess of carbon disulphide at gentle heat (better in a steam-bath), place the filter and contents in a large porcelain crucible, add 1 or 2 c. c. of nitric acid, and cover with a glass. When the violent action is over, add 4 or 5 c. c. of red fuming nitric acid, and evaporate at a gentle heat nearly to dryness to convert the sulphides into oxides. Then neutralize the remaining acid with pure sodium hydrate, wash the oxides into a silver dish with water containing a little sodium hydrate (using as little as possible), evaporate nearly to dryness, add about 8 parts of pure sodium hydrate, and a little sodium nitrate, continue the evaporation to perfect dryness, and fuse. As soon as the mass is fused, remove the heat, and when it is cool enough add 100 c. c. of hot water, and boil until the contents of the dish are pulverulent. Finally, cool, add alcohol to the amount of one third the volume of the fluid, filter, wash the residue with dilute alcohol (prepared by mixing 1 part of alcohol with 2 parts of water), to which has been added a few drops of strong solution of sodium carbonate. The insoluble sodium antimonate will remain on the filter, while the sodium stannate and sodium arsenate go into solution. Wash the antimonate from the filter into a beaker with water, place the beaker under the filter, and pour through the latter 10 or 15 c. c. of warm concentrated hydrochloric acid, containing 1 gm. of tartaric acid, wash with a little water, and warm until everything is dissolved. Dilute the solution to 100 c. c., saturate it with sulphuretted hydrogen, filter, wash, treat the precipitate as directed in the analysis of antimony ore,

and calculate the per cent of antimony. (See Fres., *Quant. Anal.*, § 165—4—a, p. 398.)

Should there be no arsenic present, acidify the filtrate containing tin with hydrochloric acid, and saturate with sulphuretted hydrogen. Heat, filter, wash with solution of ammonium acetate, containing a little free acetic acid, dry, roast at gentle heat in a weighed porcelain crucible, then heat strongly, cool, weigh the stannic oxide, and calculate the per cent of tin. (See analysis of tin ore.) Purify the weighed precipitate as in analysis of bronze. Should arsenic be present, it will be found, together with the tin, in the filtrate from the sodium antimonate, after the fusion with sodium hydrate. Add to the filtrate 1 or 2 c. c. of ammonia, and 2 or 3 c. c. of yellow ammonium sulphide, and warm gently for a short time. Then add 5 c. c. of "magnesium mixture," and allow to stand for 12 hours. Filter out the magnesium-ammonium arsenate, treat it as directed in the analysis of arsenic ore, and calculate the per cent of arsenic.

Acidify the filtrate from the magnesium arsenate with hydrochloric acid, precipitate the tin as sulphide, and proceed to determine it as directed above.

The filtrate from the lead sulphate will contain the iron. Precipitate the iron as basic acetate, filter, wash moderately, dissolve the precipitate in hydrochloric acid, re-precipitate with ammonia, filter, wash, dry, ignite, weigh the ferric oxide, and calculate the per cent of iron.

Examine the filtrate for other metals of Group IV., and, if found, determine them. (H. Will, *Anleitung f. Anal. Chem.*, 225, Ed. 1857.)

## CHAPTER XXVIII.

### REFINED LEAD.

Determine silver in separate portion. *Note 1.*

For other metals, dissolve 200 gms. in nitric acid. *Note 2.*

<i>Residue (a).</i> Sb, Sn. Add to pre- cipitate (r). <i>Note 2.</i>		<i>Solution (a).</i> Add sulphuric acid. <i>Note 3.</i>	
		<i>Residue (b).</i> PbSO <sub>4</sub> . <i>Note 3.</i>	<i>Solution (b).</i> Evaporate. <i>Note 3.</i>
<i>Precipitate (c).</i> PbSO <sub>4</sub> . <i>Note 4.</i>		<i>Solution (c).</i> Dilute and pass H <sub>2</sub> S. <i>Note 5.</i>	
<i>Filtrate (d).</i> Reject. <i>Note 4.</i>	<i>Prec. (d).</i> Add to <i>Precipitate</i> (f). <i>Note 4.</i>	<i>Solution (f).</i> Evaporate to 500 c. c. <i>Note 6.</i>	<i>Precipitate (f).</i> Sb, As, Sn, Bi, Cu, Cd, Pb. Add <i>precipitate (d)</i> . <i>Note 10.</i>
<i>Precipitate (g).</i> Fe, Zn, Co, Ni. <i>Note 7.</i>		<i>Solution (g).</i> <i>Prec. (k).</i> Add to <i>precipitate</i> (g). <i>Note 6.</i>	<i>Residue (l).</i> Bi, Cu, Cd, Pb. <i>Note 10.</i>
<i>Residue (h).</i> Co, Ni. <i>Note 7.</i>	<i>Solution (h).</i> Fe, Zn. <i>Note 8.</i>	<i>Solution (k).</i> Reject. <i>Note 6.</i>	<i>Solution (l).</i> As, Sb, Sn. <i>Note 10.</i>
<i>Prec. (i).</i> Fe. <i>Note 8.</i>	<i>Solution (i).</i> <i>Note 9.</i>	<i>Solution (m).</i> <i>Note 11.</i>	
<i>Solution (j).</i> <i>Note 9.</i>	<i>Prec. (j).</i> <i>Note 9.</i>	<i>Solution (n).</i> Cd, etc. <i>Note 11.</i>	<i>Prec. (n).</i> Bi. <i>Note 11.</i>
<i>Precipitate (o).</i> Cd. <i>Note 11.</i>		<i>Filtrate (o).</i> <i>Note 11.</i>	<i>Solution (s).</i> As, Sb, Sn. <i>Note 12.</i>
<i>Solution (x).</i> <i>Note 11.</i>		<i>Precipitate (x).</i> <i>Note 11.</i>	<i>Prec. (t).</i> As, Sb, Sn. <i>Note 12.</i>
<i>Solution (u).</i> As. <i>Note 12.</i>		<i>Residue (u).</i> Sb, Sn. <i>Notes 13 and 14.</i>	
			<i>Filtrate (t).</i> Reject. <i>Note 12.</i>

Compare Fres., *Zeit. für An. Chem.*, Vol. VIII., 1869.  
The lead may contain silver, copper, bismuth, cadmium,  
zinc, iron, nickel, cobalt, arsenic, antimony, tin, manga-  
nese.

*Note 1.*—The silver may be determined either by cupel-  
lation, or by a wet method. If the latter plan is adopted,  
weigh 200 gms. of pieces, scraped clean, introduce them

into a 1.5-litre flask, add nitric acid of 1.2 sp. gr., in small portions at a time, always keeping the metal in excess, and heat the liquid until only about 5 or 10 gms. of lead remain undissolved, and the solution begins to turn yellow in consequence of the formation of lead nitrite. The silver will be concentrated in the residual metal. Withdraw it from the solution, and dissolve it in nitric acid, dilute to 200 c. c., and add a mixture of 1 c. c. of hydrochloric acid and 50 c. c. of water. Allow the whole to stand 2 or 3 days, and after all the silver chloride has settled, draw off the clear fluid, and filter out the silver chloride, on a small filter, wash with hot water, dry, and ignite filter and precipitate together in a small weighed porcelain crucible. If the amount of silver chloride is so considerable that there is a possibility of its being incompletely reduced by the combustion of the filter-paper, the residue must be heated for a few minutes in a stream of hydrogen before weighing. The amount left, after subtracting the filter-ash, gives the quantity of silver in the 200 gms. of lead. The refined metal seldom contains more than 0.0015 per cent of silver.

Instead of treating the ignited precipitate with hydrogen, add about 0.5 c. c. of nitric acid, evaporate to dryness, again add 0.5 c. c. of nitric acid, heat to dissolve any reduced silver, add 8 or 10 drops of hydrochloric acid, evaporate to dryness, fuse the silver chloride, cool, weigh, and calculate the silver. (See analysis of barium chloride.)

*Note 2.*—For the main analysis, weigh 200 gms. of lead, cleaned as before, introduce it into a 2-litre flask, add 500 c. c. pure nitric acid of 1.2 sp. gr. and 1 litre of water, and allow it to stand for 24 hours. Should a residue (*a*) containing antimony and tin remain, filter it out, dissolve it in hydrochloric acid, dilute a little, pass sulphuretted hydrogen through the solution, filter out the precipitate, wash, and reserve it to go with precipitate (*r*), consisting of the sulphides of antimony, arsenic, and tin.

*Note 3.*—Transfer the clear solution (*a*) to the 2-litre flask,

if not already there, add 65 c. c. of pure concentrated sulphuric acid, shake, cool, fill up to the 2-litre mark, agitate again, and allow to settle. Then siphon off accurately 1750 c. c. of the clear solution, and reject the rest containing lead sulphate or residue (*b*). It has been found, by repeated experiments, that the lead sulphate from 200 gms. of lead occupies 44.99 c. c., or, in round numbers, 45 c. c. The 2-litre flask, when filled to the mark, will hold, then 1955 c. c. of solution and 45 c. c. of lead sulphate. But as 1955 c. c. of the solution correspond to 200 gms. of the lead, then 1750 c. c. of solution will correspond to 179.03 gms. of the original lead, or, in round numbers, 179 gms. Consequently, all the calculations must be based upon this as the quantity taken for analysis. Evaporate the 1750 c. c. of solution (*b*), to fumes of  $\text{SO}_3$ , allow to cool, add 60 c. c. of water, filter off and wash precipitate (*c*) of lead sulphate, containing, perhaps, a little antimony.

*Note 4.*—Dissolve precipitate (*c*) in hydrochloric acid, add 10 volumes of sulphuretted hydrogen water, warm, pass sulphuretted hydrogen gas, allow the precipitate to settle, filter, wash, spread filter in a porcelain dish, heat with a solution of yellow sulphide of ammonium or potassium, to which a little pure sulphur has been added, filter, wash, acidify the filtrate with hydrochloric acid, allow the precipitate to settle at a gentle heat, filter, and wash.

Reject the filtrate, or filtrate (*d*), and add the precipitate, or precipitate (*d*), to precipitate (*f*). If precipitate (*d*) contains much lead, treat it again with ammonium or potassium sulphide, as before, filter, acidulate with hydrochloric acid, allow the antimony sulphide to settle, filter, and add the pure antimony sulphide to precipitate (*f*).

*Note 5.*—Dilute solution (*c*), the filtrate from precipitate (*c*) of lead sulphate, to 200 c. c., heat to  $70^\circ \text{C.}$ , pass the sulphuretted hydrogen, allow to stand 12 hours over a very gentle heat, filter through a small filter, and wash with hot water. There will be a solution (*f*), which may contain iron, zinc, cobalt, nickel, and manganese, and a

precipitate (*f*), which may contain antimony, arsenic, tin, bismuth, copper, cadmium, and lead.

*Note 6.*—Evaporate solution (*f*) to a volume of about 400 c. c., transfer to a half-litre flask, make alkaline with ammonia, mix with freshly-prepared ammonium sulphhydrate, fill the flask, and allow to stand 24 hours. When the precipitate (*g*) has settled, filter, acidify the filtrate, or solution (*g*), with acetic acid, and boil to recover any nickel which may have been retained in the solution. Filter out precipitate (*k*) of nickel sulphide, and, after washing it slightly and drying, add it to precipitate (*g*), which contains the principal part of the nickel, and reject the filtrate, or solution (*k*).

*Note 7.*—Treat precipitate (*g*), containing, perhaps, iron, zinc, nickel, cobalt, and manganese, on the filter, with a mixture of 1 part of hydrochloric acid of sp. gr. 1.12, and 6 parts of sulphuretted hydrogen water, pouring back the filtrate repeatedly on the filter, to avoid increasing the volume of fluid unnecessarily. Burn the filter containing residue (*h*), after drying, together with the filter, containing precipitate (*k*), in a porcelain crucible, treat with nitro-hydrochloric acid, concentrate the solution, add a little water, filter, wash, make the filtrate alkaline with ammonia, add a few drops of ammonium carbonate, filter into a platinum dish, treat the filtrate with a few drops of strong solution of potassium hydrate, and heat until ammonia is entirely expelled. Then filter off the slight flocculent precipitate, wash, dry, ignite, and weigh the nickel oxide, and calculate metallic nickel. (See analysis of nickel ore.) Test the precipitate with the blow-pipe for cobalt.

*Note 8.*—Add a few drops of nitric acid to solution (*h*), containing the iron and zinc, concentrate, make alkaline with ammonia, filter off the ferric hydrate, or precipitate (*i*), dissolve the precipitate with a few drops of hydrochloric acid, again precipitate with ammonia, filter, wash, dry, ignite, weigh the ferric oxide, and calculate metallic iron. To verify the results, fuse the precipitate with acid



sodium sulphate, dissolve in water, reduce with zinc and platinum, and determine the iron with a dilute solution of potassium permanganate. (See analysis of ammonia-iron-alum.)

*Note 9.*—Mix solution (*i*), or the filtrate from the ferric hydrate, with a little ammonium sulph-hydrate in a small flask, and allow to stand for 24 hours in a warm place. Filter out precipitate (*j*), wash and digest on the filter with dilute acetic acid, to dissolve out any manganese sulphides. Dissolve the residue of zinc sulphides remaining on the filter with hydrochloric acid, boil, after adding a little potassium chlorate to oxidize the sulphur, precipitate the zinc with sodium carbonate, and from the ignited precipitate calculate the zinc. (See analysis of zinc ore.)

Boil solution (*j*), or the acetic acid solution of manganese sulphide, to small volume, add a little bromine water, warm until the excess of bromine is expelled, filter, wash with hot water, dry, ignite the precipitate, and calculate the manganese. (See analysis of manganese ore.)

*Note 10.*—Heat precipitate (*f*), which may contain antimony, arsenic, tin, copper, bismuth, cadmium, and lead, after adding precipitate (*f*), with a solution of potassium sulphide, to which some pure sulphur has been added, filter out residue (*l*), which may contain bismuth, copper, cadmium, and lead, and wash with hot water. Acidulate the filtrate, or solution (*l*), which may contain arsenic, antimony, and tin, with hydrochloric acid, and allow the precipitate to settle completely. Filter out precipitate (*r*), which may contain arsenic, antimony, and tin, and reject the filtrate, or solution (*r*).

Heat residue (*l*), (insoluble in potassium sulphide) nearly to boiling, in a porcelain dish, with dilute nitric acid (prepared by mixing 1 part of acid of 1.2 sp. gr. with 12 parts of water). When the precipitate is dissolved, filter, wash the paper slightly, dry, ignite it, and add the ash to the nitric-acid solution. Then add 2 c. c. of dilute sulphuric acid, evaporate to fumes of  $\text{SO}_3$ , dilute a little, and filter

out and wash precipitate (*m*) of lead sulphate, which may be rejected. (See analysis of galena.)

*Note 11.*—Nearly neutralize solution (*m*) (or the filtrate from the lead sulphate, and which may contain bismuth, copper, cadmium, and silver), with pure potassium hydrate, add  $\text{Na}_2\text{CO}_3$  and a little of a solution of pure potassium cyanide free from potassium sulphide, and heat gently. If a precipitate (*n*) of bismuth hydrate is produced, filter it out, wash, dissolve it in dilute nitric acid, precipitate it with ammonium carbonate, weigh it as bismuth trioxide ( $\text{Bi}_2\text{O}_3$ ), and calculate the metallic bismuth. (See *Fres., Quant. Anal.* § 120.) To solution (*n*) add a little more potassium cyanide and a few drops of potassium sulphide, filter and wash the precipitate (*o*) of sulphides of cadmium and silver, dissolve in dilute nitric acid, add a little hydrochloric acid, filter out and wash the precipitate of silver chloride or precipitate (*x*), which may be rejected, as the silver is determined elsewhere. Evaporate solution (*x*), containing cadmium, nearly to dryness, add a few drops of solution of sodium carbonate, filter out the precipitate of cadmium carbonate, wash, dry, ignite, and weigh the cadmium oxide, and from it calculate metallic cadmium. To prevent reduction and volatilization of cadmium during the ignition, moisten the filter with solution of ammonium nitrate.

If no precipitation of the cadmium is produced by the sodium carbonate, add a little potassium hydrate, and if one then forms, filter, wash, and proceed as above. Mix the filtrate from the sulphides of silver and cadmium, or filtrate (*o*), with a small quantity of nitric and sulphuric acids, and evaporate nearly to dryness. Then add a few drops of hydrochloric acid, and heat until cyanogen is expelled. Filter, if necessary, and determine the copper by one of the methods given in the analysis of copper ore.

When cadmium is absent, the separation of the bismuth and copper may be effected by means of ammonia and ammonium carbonate, removing any silver by hydrochloric

acid before precipitating copper sulphide. (For precautions to be observed, see Fres., *Quant. Anal.*, § 163, 5.)

*Note 12.*—To precipitate (*r*), which may contain arsenic, antimony, and tin, and which was obtained by acidifying the potassium sulphide solution (*l*) with hydrochloric acid, add the sulphuretted hydrogen precipitate from the solution of residue (*a*), (see *Note 2*), dry, and treat repeatedly with carbon disulphide. After the carbon disulphide has evaporated from the filter, warm it, with its contents, in a covered porcelain crucible, after adding a few drops of red fuming nitric acid, heat the solution cautiously to expel excess of nitric acid, add sodium carbonate in excess and a little sodium nitrate, evaporate to dryness, and heat until the mass melts, and becomes white. Transfer the fused mass to a small mortar, add a little water, and pulverize carefully. Then wash it into a breaker, and proceed as directed in the analysis of type metal. (See also Fres., *Quant. Anal.*, page 427.)

Dissolve residue (*s*) of sodium antimonate, in hydrochloric and tartaric acids, pass sulphuretted hydrogen, set aside for a few hours, filter out antimony sulphide, wash, dry the precipitate, and reserve it to be combined with the sulphuretted hydrogen precipitate from the solution of residue (*u*).

Evaporate solution (*s*), which may contain arsenic, antimony, and tin, in order to expel alcohol, add excess of dilute sulphuric acid, evaporate to expel nitric acid, add water, heat to 70° C., and pass sulphuretted hydrogen. When precipitate (*t*) has settled, filter, and wash with water, and reject the filtrate, or solution (*t*). If no tin be present, treat precipitate (*t*), on the filter, with a cold concentrated solution of ammonium carbonate, pouring the filtrate back on the filter repeatedly in order to avoid the use of a large excess of solution of ammonium carbonate. The ammonium carbonate solution (*u*) will contain the arsenic. Acidulate it with hydrochloric acid, add a little filtered sulphuretted hydrogen water, filter through a

small tube, in which a little asbestos has been placed, both having been previously heated and weighed. When the whole of the precipitate has been transferred to the little tube, heat it at  $100^{\circ}$  C., until the greater portion of the water is expelled, and then heat it gently, not much above  $100^{\circ}$  C., in a stream of dried carbon dioxide, allow it to cool in a current of the gas, displace the carbon dioxide with atmospheric air, and weigh the tube and contents, and, from the trisulphide, calculate the arsenic. A better plan is to filter out the arsenious sulphide on a very small filter, oxidize the filter and sulphide together by evaporation with fuming nitric acid, fuse the residue in platinum with a little sodium carbonate and nitrate, dissolve in water, and weigh the arsenic as magnesium pyro-arsenate, as directed in the analysis of arsenic ore.

*Note 13.*—Dissolve residue (*u*) containing antimony, together with the precipitate from solution of residue (*s*), in strong hydrochloric acid, pass sulphuretted hydrogen, filter through a small tube in the same way as directed above in the case of arsenic, heat gently in a stream of dried carbon dioxide, until the antimony trisulphide turns black, cool in a current of the gas, displace the latter by a current of dry air, weigh the tube and contents, and calculate the antimony. Or, oxidize the antimony oxide by Bunsen's method with nitric acid, and weigh it, as directed in the analysis of antimony ore, as antimony tetroxide.

*Note 14.*—If tin be present, after expelling alcohol, passing sulphuretted hydrogen, and filtering out the precipitate, dissolve the latter in potassium sulphide, add excess of sulphurous acid, digest for some time on a water-bath, and then boil until two thirds of the water, and all the sulphurous acid are expelled. Solution (*t*) will contain all the arsenic. (See Bunsen, in *Annal. d. Chem. u. Pharm.*, 106, 3, and Fres., *Quant. Anal.*, § 165-6.)

Precipitate the arsenic as sulphide, oxidize, fuse, take

up with water, and weigh the arsenic as magnesium pyroarsenate, as directed in the analysis of arsenic ore.

Residue (*t*) will contain the tin and antimony. Oxidize it with fuming nitric acid in a weighed porcelain crucible, and weigh. Then ignite in a stream of hydrogen to expel the antimony tetroxide, oxidize again with nitric acid, and weigh the stannic oxide, from which calculate the tin. Calculate the antimony from the loss of antimony tetroxide. The tin and antimony may be separated and determined by oxidizing the residue left after extracting the arsenic, with nitric acid, fusing, dissolving in water, filtering out the soluble stannate from the insoluble antimonate, which latter is to be dissolved in hydrochloric and tartaric acids, precipitated as sulphide, and the sulphide oxidized and weighed as antimony tetroxide, as directed in the analysis of antimony ore.

To determine the tin, precipitate the sulphide from the solution of stannate, by means of sulphuretted hydrogen, filter it out, and burn it to stannic oxide, as directed in the analysis of tin ore.

*Note 15.*—To determine the small quantity of sulphur which may be present in the lead, draw out a piece of combustion tubing about 1 metre long, and of about 2 centimetres diameter, to a long point, which is bent down so as to dip into a small 3-bulbed U tube filled with water. Also narrow the combustion tube in the middle, so as to form a kind of bridge. Introduce into the anterior end of the tube about 100 gms. of the lead, in the form of a rod of about 1 centimetre diameter, close the tube with a common cork, connect it with a smaller tube containing fragments of charcoal, and place it in a combustion furnace. Then heat the charcoal to the point of ignition, and pass a current of chlorine. When the tubes are filled with chlorine, melt the lead carefully, the tube being so inclined that the melted lead will flow against the bridge, but not over it, and not flow back against the cork. Keep the charcoal red hot to remove any oxygen from the

chlorine. Regulate the heat so that the lead will burn slowly to lead chloride, and collect in the empty part of the tube. If the stream of chlorine is properly regulated, and the lead chloride not heated, very little of it will pass over into the U tube. Wash the contents of the U tube into a beaker, precipitate the  $\text{SO}_2$  with barium chloride as usual, and calculate the sulphur.

## CHAPTER XXIX.

### WHITE PAINT GROUND IN OIL.

Extract the oil. *Note 1.* The dry paint may contain  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{CaSO}_4$ ,  $2\text{PbCO}_3$ — $\text{PbH}_2\text{O}_2$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{ZnO}$ ,  $\text{PbO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2(\text{SiO}_3)_3$ . *Note 2.*

<i>Residue (a).</i> $\text{BaSO}_4$ , $\text{PbSO}_4$ , $\text{CaSO}_4$ , $\text{SiO}_2$ , $\text{Al}_2(\text{SiO}_3)_3$ . <i>Note 3.</i>		<i>Solution (a).</i> $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ , $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ . <i>Note 9.</i>	
<i>Residue (b).</i> $\text{BaSO}_4$ , $\text{PbCO}_3$ , $\text{CaCO}_3$ , $\text{SiO}_2$ , $\text{Al}_2(\text{SiO}_3)_3$ . <i>Note 4.</i>	<i>Filtrate (b).</i> $(\text{NH}_4)_2\text{SO}_4$ . It may be rejected. <i>Note 8.</i>	<i>Precipitate (e).</i> $\text{PbS}$ , $\text{ZnS}$ . <i>Note 9.</i>	<i>Filtrate (e).</i> $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ , $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ . <i>Note 11.</i>
<i>Residue (c).</i> $\text{BaSO}_4$ , $\text{SiO}_2$ , $\text{Al}_2(\text{SiO}_3)_3$ . <i>Notes 5 and 6.</i>	<i>Solution (c).</i> $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ . <i>Note 7.</i>	<i>Res. (f).</i> $\text{PbSO}_4$ . <i>Note 9.</i>	<i>Filt. (f).</i> $\text{ZnSO}_4$ . <i>Note 10.</i>
<i>Precipitate (d).</i> $\text{PbS}$ . <i>Note 7.</i>	<i>Solution (d).</i> $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ . <i>Note 8.</i>	<i>Prec. (g).</i> $\text{BaSO}_4$ . <i>Note 11.</i>	<i>Filt. (g).</i> $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ . <i>Note 12.</i>

The paint may contain, besides the oil, one or more of the following constituents, namely: Sulphates of lead, barium, and calcium; carbonates of lead, barium, and calcium; oxides of lead and zinc, and also silica and clay.

Make a careful qualitative analysis of the paint, after extracting the oil, for upon it will depend the character of the quantitative analysis.

*Note 1.*—Weigh a clean dry flask, which holds about 150 c. c., and introduce into it 3 or 4 gms. of the paint, and note the weight. Then add 30 or 40 c. c. of ether or gasoline, shake well, and heat over steam until the fluid boils. Allow the solid matter to settle, and decant the clear fluid on a dry filter without disturbing the residue more than is necessary. Repeat the operation with 25 or 30 c. c. of the solvent. Finally, wash the contents of the

flask on the filter with 25 or 30 c. c. of ether or gasoline, and dry the filter and contents, in an air-bath, at 100° C. The quantitative analysis may be made of a portion of this.

To determine the oil, evaporate the filtrate in a weighed dish, without application of heat, until only oil is left, and then in an air-bath, at a temperature of 100° C., for about an hour, cool, and weigh. Should there be any water in the oil, as there may be, if the ether used was not perfectly anhydrous, continue to heat at 100° C. until it is expelled, and then cool and weigh. Should the filtrate be turbid, and not cleared by refiltering, as is sometimes the case, pour it into a measured flask, dilute to a known volume, dilute with ether or gasoline, as the case may be, cork, and set it aside. After the solid matter has settled, take an aliquot portion of the clear fluid, evaporate it in a weighed dish, as directed above, and calculate the per cent of oil. The proportion of solid matter will be too small to render it necessary to make the allowance for its volume, as in the case of refined lead.

*Note 2.*—Weigh carefully 1 gm. of the dry residue, from which the oil has been thoroughly extracted, and dissolve it in about 25 c. c. of hot acetic acid, in a covered vessel. Filter, and wash with hot water.

If there be any residue (*a*) left on the filter, it will contain the silica and clay, and sulphates of barium calcium and lead, that may be present in the paint.

Solution (*a*) may contain lead, zinc, calcium and barium in the form of acetates, the last being due to the use of witherite (barium carbonate).

*Note 3.*—Treatment of residue (*a*):

Wash it from the filter into a beaker with water, add 8 or 10 gms. of ammonium carbonate, plug the point of the funnel, and fill also with a strong solution of ammonium carbonate, placing it in a filter-stand over the beaker, and allow all to stand for 12 hours, with frequent stirring. By this means, the sulphates of lead and calcium will be



converted into carbonates, while the barium sulphate, silica, and clay will remain unaltered. Then remove the plug from the point of the funnel, allow the fluid in the filter to run through into a second beaker, pour the solution of ammonium carbonate, from the first beaker, on the same filter, also transfer to it residue (b) (which may contain sulphate of barium, carbonates of calcium and lead, and silica and clay), and wash well with hot water. The filtrate and washings, or filtrate (b), will contain the sulphuric acid, which was combined with calcium and lead, and may be rejected. (See note on galena analysis, p. 144.)

*Note 4.*—Pour through the filter containing residue (b) (or the carbonates of calcium and lead, the sulphate of barium, and the silica and clay), hot acetic acid until it produces no effervescence, and wash well with water.

Residue (c) will contain any sulphate of barium, silica, and clay, while filtrate (c) will contain any acetates of lead and calcium.

*Note 5.*—Dry, ignite, and weigh residue (c). Then fuse it with sodium carbonate, boil the fused mass in water, filter, and wash out alkaline sulphate. Treat the residue, containing barium carbonate, with hot dilute hydrochloric acid, by pouring it through the filter, and wash the latter well with hot water, allowing the filtrate and washings to run together into a separate beaker. To the clear acid solution add sulphuric acid, and determine the barium sulphate as usual. This will give the amount of *barytes* in the paint. The difference between this weight and that of the total residue (c) will give the amount of silica and clay.

*Note 6.*—Evaporate nearly to dryness the filtrate from the barium sulphate, after washing into it any residue left upon the filter, after dissolving the barium carbonate, transfer to a platinum crucible, add some acid sodium sulphate, and fuse. When the mass is cool enough, add a little sulphuric acid, heat until the mass is brought to a pasty consistence, cool, and dissolve in water. By this

means, the silica will be rendered insoluble, and the alumina dissolved. Filter out and weigh the silica; precipitate the alumina with ammonia, and determine it as usual. Calculate the alumina to clay ( $\text{Al}_2(\text{SiO}_3)_3$ ). Any excess of silica is probably due to the use of infusorial earth.

*Note 7.*—Saturate the filtrate from the barium sulphate, clay, and silica, or acetic acid solution (*c*), with sulphuretted hydrogen, filter out the lead sulphide, or precipitate (*d*), and wash it with a little sulphuretted hydrogen water. Then wash the precipitate from the filter into a beaker, dry the filter, transfer it to a porcelain crucible, moisten it with nitric acid, burn it, add the ash to the precipitate, and dissolve all with nitric acid. Then add a little concentrated sulphuric acid, evaporate to fumes  $\text{SO}_3$ , dilute, filter out, and determine the lead sulphate existing as such in the paint. (See analysis of galena.)

*Note 8.*—Boil out the sulphuretted hydrogen from the filtrate from the lead sulphide, or solution (*d*), which may contain calcium acetate, add excess of ammonia and ammonium oxalate, filter, treat the precipitate as directed in the analysis of calcite, and weigh the calcium sulphate which existed in the paint as such.

*Note 9.*—Treatment of solution (*a*):

Solution (*a*) may contain acetates of lead, zinc, calcium, and barium. Saturate with sulphuretted hydrogen, filter out, and wash precipitate (*e*), which may contain sulphides of lead and zinc, dissolve the precipitate in nitric acid, add sulphuric acid to the solution, evaporate to fumes of  $\text{SO}_3$ , dilute, filter out the lead sulphate, or residue (*f*), observing the directions given in the analysis of galena, and calculate to basic carbonate of lead ( $2\text{PbCO}_3, \text{PbH}_2\text{O}_2$ ). (See *Note 13*.)

*Note 10.*—From filtrate (*f*), the filtrate from the lead sulphate, precipitate the zinc with excess of sodium carbonate, and determine the zinc oxide, as in the analysis of zinc ore.

After precipitating, and filtering out the zinc carbonate, treat the filtrate with sulphuretted hydrogen, to insure

the complete precipitation of the zinc. Should any zinc sulphide be precipitated, dissolve it in hydrochloric acid and potassium chlorate, precipitate with excess of sodium carbonate as above, and, after determining the amount of zinc oxide, add it to the first.

*Note 11.*—To the filtrate from the sulphides of lead and zinc, or filtrate (*e*), which may contain acetates of calcium and barium, add a little hydrochloric acid, and dilute sulphuric acid, to precipitate any barium present, filter out the barium sulphate, and wash it with sodium hyposulphite, to dissolve out any calcium sulphate which may possibly be present. Weigh the barium sulphate, and calculate it to barium carbonate.

*Note 12.*—To the filtrate from barium sulphate, or filtrate (*g*), add excess of ammonia, and a sufficient quantity of solution of ammonium oxalate, filter wash, dry, convert the calcium oxalate into sulphate as directed in the analysis of calcite, and calculate to calcium carbonate.

*Note 13.*—In case there should be any lead oxide in the paint not combined with carbonic or sulphuric acid, it will be in the acetic acid solution (*a*), in which case a careful determination of the carbonic acid must be made, and, after subtracting enough to satisfy the calcium existing as calcium carbonate, the remainder should be calculated to basic carbonate of lead. Should there be any lead left unsatisfied, it is to be calculated to lead oxide. It must be remembered, however, that lead sulphate is slightly soluble in acetic acid, and a slight excess of lead in solution (*a*) may be due to this cause.

*Appendix 1.*—If the qualitative analysis shows the absence of sulphates of barium, lead, and calcium, should there be any residue left, after dissolving the paint in acetic acid, dry, ignite, and weigh it, as it is probably silica or clay, or both. Then fuse it with acid sodium sulphate, digest the fused mass with sulphuric acid, dissolve in water, filter out the silica, and in the filtrate determine the alumina, and calculate the clay and free silica as in *Note 6*.

If no silica or clay, or sulphates of barium, lead, or calcium be present, acetic acid will dissolve the paint to a clear solution, for the analysis of which proceed as directed in *Notes* 9, 10, 11, and 12.

If no silica, or clay, or salts of calcium and barium be present, but only carbonate of lead and oxide of zinc, the paint may be dissolved in dilute nitric acid, and the solution, after adding sulphuric acid, treated for lead, as directed in analysis of galena; the lead calculated to basic carbonate (white lead), and the zinc precipitated from the filtrate by sodium carbonate, determined as in the analysis of zinc ore, and calculated to oxide.

If the paint be a pure lead paint, dissolve in nitric acid, and determine the lead by evaporating with sulphuric acid, and proceeding as directed in the analysis of galena. The lead is to be calculated to basic carbonate.

If it be a simple zinc paint, dissolve in nitric acid, precipitate the zinc directly with sodium carbonate, and weigh it as oxide, as in analysis of zinc ore.

In all cases where zinc is precipitated by sodium carbonate, treat the filtrate with sulphuretted hydrogen, and if any zinc sulphide be recovered, filter it out, dissolve in hydrochloric acid, precipitate with sodium carbonate, and add the precipitate to the first one.

*Appendix 2.*—In paint composed of sulphate and oxide of lead, and containing no carbonate, after dissolving in acetic acid, filtering, and washing well, dry, ignite as directed in analysis of galena, and weigh the lead sulphate.

In the acetic acid solution, determine both the lead and sulphuric acid, as a small amount of lead sulphate may be dissolved by the acetic acid. Calculate the sulphuric acid to lead sulphate, and add it to that found in the residue. Deduct the amount of lead due to lead sulphate, from the total lead found in the acetic acid solution, and calculate the remainder to lead oxide ( $\text{PbO}$ ), existing as such in the paint.

## CHAPTER XXX.

### FRESH WATER.

The kind of analysis required depends upon the use to be made of the water, whether for drinking and general domestic purposes, for steam boilers, for manufacturing purposes, or as a mineral water.

The determination of its value as a potable water can be made by a short and simple analysis, showing the amount of silica, alumina, and oxide of iron, lime, magnesia, soda, potash, chlorine, sulphuric acid, organic and volatile matter (expelled by ignition from the residue left after evaporating a given quantity of water), and ammonia, both free and in a form styled albuminoid, which latter is thought to indicate constituents very detrimental to health. Besides, it is important to know its hardness, or soap destroying power.

This analysis will furnish all the information that is requisite to estimate the fitness of water for use in steam boilers, and for manufacturing purposes.

The analysis of mineral water is much more complicated and laborious, and will be described later.

*Organic and Volatile Matter.*—Evaporate 250 c. c. of the water to dryness, in a weighed platinum dish, first on a water-bath, and then in an air-bath at  $130^{\circ}$  C., and reweigh the dish with its contents. Then heat the dish, at low-red heat, until all organic matter is consumed, and the contents are white or nearly so. Then add 25 c. c. of water, saturated with carbon dioxide, evaporate to dryness on a water-bath, repeat the treatment with carbon dioxide, evaporate on a water-bath, dry in an air-bath at  $130^{\circ}$  C., as before, cool, and weigh. The difference between this weight and the first expresses the amount of *organic and volatile matter* in the quantity of water taken.

In this country it is customary to report analysis of water as made on 1 U. S. gallon of 231 cubic inches, containing a certain number of grains, which number has been fixed upon in the Columbia College School of Mines as 58,318. The weights and measures used are French. This involves a short calculation to convert milligrammes into the corresponding number of grains. One milligramme is one millionth of 1 litre. Suppose that upon evaporating 1 litre of water 1 milligramme of solid matter was left, the quantity will be one millionth of 1 litre. If a gallon of the same water were used, the solid matter would amount to one millionth of 1 gallon, or, as the gallon is assumed to contain 58,318 grains, one millionth of 58,318, and any number of milligrammes will correspond to that number of millionths of 58,318 grains. Therefore, the number of milligrammes multiplied by 58,318 and divided by 1,000,000 will give the number of grains in 1 U. S. gallon of 231 cubic inches. This rule applies to the calculation of all the constituents found by analysis. Then, to determine the number of grains of *organic and volatile matter* in 1 gallon of the water under examination, calculate the number of milligrammes which would be lost by treating the residue left after evaporating 1 litre of the water as directed above, multiply this by 58,318, and divide by 1,000,000. The difference between the weight of dry residue before ignition and the sum of the constituents found by analysis, allowing for the loss of the water and part of the carbonic acid of acid carbonates, should not amount to more than a small fraction of a grain. If it does, the analysis should be repeated. This remark applies only to water containing a small amount of mineral matter. In the analysis of mineral waters, if it is desired to determine the "total solids" as a check on the correctness of the analysis, another method is pursued, which will be explained later.

*Silica, Lime, Magnesia, Alumina, and Oxide of Iron.*—To determine these, evaporate in a platinum dish nearly

to dryness on a sand-bath (finishing the evaporation to dryness on a water-bath), from 2 to 8 litres of water, according to the purity of the water, having previously acidulated it with hydrochloric acid. Then dry the residue in an air-bath at  $110^{\circ}$  C., until the odor of hydrochloric acid cannot be detected, and proceed exactly as directed in the analysis of limestone. For this part of the analysis of Croton water, 5 litres will be sufficient. The evaporation may be made in porcelain instead of platinum, but there is danger of introducing a small amount of silica and alumina into the analysis. As in the analysis of water of this character it is unnecessary to separate the small amount of alumina and oxide of iron, they are generally weighed together, and reported as alumina and ferric oxide.

*Sulphuric Acid.*—Acidulate from 1 to 4 litres of the water with hydrochloric acid, evaporate to about 100 c. c., filter, if necessary, and determine  $\text{SO}_3$  as in analysis of magnesium sulphate. For this determination in Croton water, 2 litres will be sufficient.

*Chlorine.*—Evaporate from 1 to 4 litres of the water to about 100 c. c. (2 litres of Croton water will be sufficient), and determine the chlorine volumetrically, by means of a standardized solution of silver nitrate. The determination is made by first adding to the water 3 drops of a saturated solution of potassium chromate, and then dropping into it the solution of silver nitrate, from a burette, until the red color of silver chromate appears. The number of c. c. of silver nitrate solution used, multiplied by the value of 1 c. c., will give the amount of chlorine. This is calculated to grains in a gallon as above. The solution of silver nitrate is prepared by dissolving it in distilled water, in the proportion of 17 gms. of the pure salt in 1 litre of water. To standardize the silver nitrate solution, dissolve 1 gm. of pure fused sodium chloride in 1 litre of distilled water, pour exactly 100 c. c. of the solution into a beaker, add 3 drops of saturated solution of potassium chromate,

and drop in, from a burette, the silver solution until the red color of silver chromate appears. The known quantity of chlorine, in the 100 c. c. of salt solution, divided by the number of c. c. of silver solution used, will give the value of 1 c. c. of the latter. In the analysis of water containing very little chlorine, it is well to use a *centime* silver nitrate solution. To prepare this, run 10 c. c. of the strong solution into a flask holding exactly 100 c. c., fill with water to the holding mark, and mix well.

*Soda and Potash.*—Evaporate from 1 to 10 litres to about 100 c. c. according to the character of the water (5 litres of Croton water will be enough), acidulate slightly with hydrochloric acid, then add saturated solution of barium hydrate until the fluid is strongly alkaline, boil, filter, and wash well with hot water, to remove chlorides. From the filtrate precipitate excess of barium, by adding ammonium carbonate as long as it produces a precipitate, and boiling. Filter and wash the precipitate of barium carbonate with hot water until the washings give no reaction for chlorine. Evaporate the filtrate to dryness, and burn out the ammonium chloride at low-red heat. Take up with water, and repeat the treatment with barium hydrate, and ammonium carbonate, to insure the complete removal of magnesium, which may have been kept in solution by the alkaline chlorides. Finally, evaporate the filtrate to dryness in a weighed dish (preferably of platinum), expel any ammonium chloride present, at low red heat; cool and weigh the chlorides of sodium and potassium. Dissolve the contents of the dish with water, and determine the potassium, as directed in the analysis of potassium alum, and calculate the sodium. Consult analysis of feldspar.

*Hardness.*—By this is meant the soap-destroying power of the water. A degree of hardness means the effect produced on a solution of soap by water containing 1 grain of calcium carbonate in a gallon. For the determination, there will be required a solution of soap, and one of cal-



cium chloride, with which to standardize the solution of soap.

*Soap Solution.*—To prepare this, dissolve 10 gms. of good soda soap (containing about 12 per cent of water), in 1 litre of 90 per cent alcohol; filter, and keep the solution in a glass-stoppered bottle, and mark it *Strong soap solution*. For use, add to 100 c. c. of the strong solution 100 c. c. of water, and 33 c. c. of alcohol, adding the alcohol before the water, and shaking *gently*, to avoid lathering.

*Calcium Chloride Solution.*—To prepare this, dissolve 1 gm. of calcium carbonate in dilute hydrochloric acid, evaporate to dryness on a water-bath, to expel all free acid, and dissolve the residue in 1 litre of distilled water. One c. c. of this solution will correspond to one mgm. of calcium carbonate. Dilute 10 c. c. of the solution to 100 c. c., with distilled water, introduce the mixture into a narrow glass-stoppered bottle, which holds about 150 c. c., and drop in the soap solution from a burette, little by little, introducing the stopper into the bottle, and shaking after each addition of soap. Continue the operation until a permanent lather is formed, which will remain unbroken for 5 minutes. The lather should not be thick and frothy, but only a light pellicle covering the surface of the solution. When it breaks, the fluid below will appear in patches. As the number of milligrammes of calcium carbonate in the fluid is known, when the number of c. c. of soap solution required to form a permanent lather is also known, a very simple calculation will give the number of milligrammes that 1 c. c. of the soap solution is equivalent to.

To determine the hardness of a sample of water, introduce into a similar bottle 100 c. c. of the water, and treat it with soap solution in the same way as directed for standardizing the latter. The number of c. c. of soap solution required, multiplied by the value of 1 c. c., and this product multiplied by 10, will give the number of milligrammes of calcium carbonate in the litre that the hardness of the water is equivalent to. This number of milli-

Calcic  
Chloride  
Sol'n

grammes multiplied by 58,318, and divided by 1,000,000, will give the corresponding number of grains of calcium carbonate in 1 gallon, or *degrees of hardness*. The hardness of water may be due to the presence of carbonates or sulphates, or, though rarely, to the presence of free acid. If it is desired to determine the "permanent" hardness, introduce into a flask holding about 250 c. c., 100 c. c. of the water, and boil for half an hour, to precipitate the carbonates held in solution by carbonic acid, make the solution up to 100 c. c., with distilled water, and determine the hardness as before. This is what is called "permanent" hardness. The difference between this and the hardness of the water, before boiling, is called "temporary" hardness. To avoid much loss by evaporation while boiling, it is well to insert into the mouth of the flask a cork, through which passes a piece of glass tubing, about 3 feet long, which has a small bulb blown in it. By this means the steam will condense and run back into the tube. The quantity of water tested should not contain more than 12 milligrammes of calcium carbonate. If it does, take a smaller quantity, dilute with distilled water to 100 c. c., and proceed as before.

This determination is valuable, as it will often obviate the necessity of an analysis to decide upon the fitness of water for manufacturing purposes, and particularly for use in steam-boilers.

*Permanganate Test* (*vid.* W. A. Miller, *Jour. Lon. Chem. Soc.*, 1865, XVIII., p. 117).—This test is made to determine the amount of oxidizable organic matter in water, and is claimed by some able chemists to be equal in value to the determination of albuminoid ammonia. Dissolve 0.7875 gm. of crystallized oxalic acid in 1 litre of distilled water; then 1 c. c. of the solution will be equivalent to one tenth of a milligramme of oxygen, as 0.7875 gm. of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) requires 0.100 gm. of oxygen to become carbonic acid ( $\text{CO}_2$ ). Then dissolve 0.500 gm. of potassium permanganate in 1 litre of water, and

dilute until 1 c. c. of the solution oxidizes 1 c. c. of the oxalic acid solution. Then 1 c. c. of the potassium permanganate solution carries one tenth of a milligramme of available oxygen. To 200 c. c. of the water add 3 c. c. of dilute sulphuric acid, and permanganate solution until the color ceases to disappear for three hours. From the number of c. c. of permanganate used, calculate the quantity of oxygen required to oxidize organic matter. It is assumed that the oxygen required, multiplied by 8, is equivalent to organic matter. (See Tidy's analysis of London water, *Reports to Local Government Board on Metropolitan Water*, 1878.)

*Free and Albuminoid Ammonia.*—The determination of these requires what is known as Nessler's solution; also a solution of ammonium sulphate or chloride for comparison, a strong solution of sodium carbonate, one of potassium permanganate, and also distilled water free from ammonia. (See *Water Analysis*, Wanklyn & Chapman, 4th Ed., London, 1876, pp. 20 *et seq.*)

*Nessler's Solution.*—To prepare this solution, dissolve 50 gms. of potassium iodide in a small quantity of hot water, place the solution on a boiling water-bath, add, with frequent agitation, a strong aqueous solution of mercuric chloride (40 gms. of the salt and 300 c. c. of water), until the red precipitate just redissolves, filter, add to the filtrate a strong solution of 200 gms. of potassium hydrate, filter, dilute to one litre, add 5 c. c. of a saturated solution of mercuric chloride, allow the precipitate formed to settle, decant the clear fluid, and keep it for use in a tightly corked bottle.

*Ammonium Solution for Comparison.*—Dissolve 0.3883 gm. of ammonium sulphate, or 0.315 gm. of ammonium chloride, in 1 litre of water, and 1 c. c. of either solution will contain one tenth of a milligramme of ammonia ( $\text{NH}_3$ ). For use dilute to ten volumes, and then 1 c. c. will contain one hundredth of a milligramme of ammonia.

*Sodium Carbonate Solution.*—Add 100 gms. of sodium

*Nessler's Solution*

*Ammonium Solution*

carbonate to 200 c. c. of distilled water free from ammonia, and keep in a well-corked bottle.

*Potassium Permanganate Solution.*—Dissolve 200 gms. of potassium hydrate and 8 gms. of crystals of potassium permanganate in 1 litre of distilled water free from ammonia, boil hard for half an hour in a two-litre flask, to expel ammonia, and keep in a well-corked bottle.

*Distilled Water.*—Boil distilled water, after adding a little sodium carbonate, in a large flask, until about one fourth is evaporated, then distill the remainder from a retort holding about 1500 c. c., until the distillate gives no reaction for ammonia with Nessler solution, testing 50 c. c. of the water at a time. When no more ammonia can be detected, distill off into a large bottle about 750 c. c., and test again, to be sure that the 750 c. c. are free from ammonia. Proceed in the same way until enough is prepared, and keep the pure water in tightly-corked bottles.

Before using the solutions of sodium carbonate and potassium permanganate, they should be tested for ammonia. Introduce into a retort, holding 1500 c. c., 1 litre of water, add 15 c. c. of the solution of sodium carbonate, and 50 c. c. of the potassium permanganate solution, and distill until the distillate gives no reaction for ammonia. Then distill 500 c. c. of the water, which will be free from ammonia. Introduce this water into a clean retort, add 15 c. c. of the solution of sodium carbonate, and distill until the distillate ceases to give a color upon the addition of Nessler solution, and determine the ammonia as directed later, and note the amount upon the bottle. Then add 50 c. c. of the potassium permanganate solution, and proceed in the same way, marking the amount of ammonia found upon the bottle. The solutions should be tested frequently.

X *Free Ammonia.*—Connect a retort (of capacity of at least 1 litre) with a good condenser, cleanse by distilling some clean water in them, introduce 500 c. c. of the water to be tested and 15 c. c. of the  $\text{Na}_2\text{CO}_3$  solution; distill, collect-

ing the distillate in test cylinders. Meanwhile place in other cylinders of the same calibre, amounts of the standard  $\text{NH}_3$  solution containing respectively 0.01, 0.02, etc., mgm.  $\text{NH}_3$ , and dilute each up to 50 c. c. When 50 c. c. have distilled over, add 1.5 c. c. of Nessler solution to each cylinder. Always use the same Nessler solution, and the same amounts, and allow it to act as nearly as possible for the same length of time. After a few minutes compare the tint of the distillate with those of the comparison cylinders, and thus estimate the amount of ammonia present therein. If the water is likely to contain much ammonia, it will be safer to mix the distillate by stirring, take out 10 c. c., dilute to 50 c. c., and test as described above. The remaining four fifths of the distillate may be used to confirm the results thus obtained. Test each succeeding 50 c. c. of the distillate in the same way, and proceed until 50 c. c. contain less than 0.01 mgm.  $\text{NH}_3$ . The whole amount of ammonia thus determined, less that due to the 15 c. c.  $\text{Na}_2\text{CO}_3$  gives *free ammonia*.

X *Albuminoid Ammonia*.—When the distillation with  $\text{Na}_2\text{CO}_3$  fails to show ammonia, add 50 c. c. of the permanganate solution and distill, testing each successive 50 c. c. of the distillate as before, until it contains less than 0.01 mgm.  $\text{NH}_3$ . Deduct ammonia due to permanganate, and the result is albuminoid ammonia.

A modification, which avoids corrections for ammonia in the reagents, may be stated briefly thus : Distill 200 to 300 c. c. of clean water with 15 c. c.  $\text{Na}_2\text{CO}_3$  until the distillate is free from ammonia ; add 500 c. c. of the water and distill, testing the distillates for *free ammonia* ; add 50 c. c. permanganate solution and again distill clean ; then 500 c. c. of the water, and test distillates for *total ammonia*. The difference between *free* and *total* gives *albuminoid ammonia*.

*Nitrates* (*vid.* Gladstone and Tribe, *Jour. Lon. Chem. Soc.*, June, 1873).—Evaporate 2 or 3 litres of the water to dryness on a water-bath after adding a small piece of caustic lime, heat the mass with 5 or 6 c. c. of distilled

water, and rinse it into a 200 c. c. flask, connected with a small Liebig condenser, which is also connected by means of a glass tube, with another small flask. The latter flask is provided with a doubly-perforated cork, through one hole of which passes the tube from the condenser, and through the other a bent glass tube connected with a small U tube containing a little broken glass, and a few c. c. of dilute hydrochloric acid. A little thin sheet zinc (10 or 15 gms.) is then plated with copper by immersing it in a concentrated solution of copper sulphate for 15 minutes, and introduce (after washing it with cold water) into the flask with the residue. The liquid in the flask is gradually heated to boiling, and distilled for about an hour. The distillate and washings of the receiver are then evaporated with platinum tetrachloride, and from the spongy platinum the nitric acid calculated. (Compare analysis of ammonio-ferric sulphate.)

*Grouping the Constituents Found by Analysis.*—It is almost impossible to give rules for grouping the constituents so as to meet all cases. It will be sufficient to give directions for grouping the results of analysis of such water as is at all likely to be used for drinking or manufacturing. Combine the sodium with chlorine as sodium chloride, and the potassium with sulphuric acid as potassium sulphate. Should there be any more sodium than the chlorine will satisfy, and more sulphuric acid than is required by the potassium, combine the excess of sodium with sulphuric acid as sodium sulphate, and should there be more sodium than the sulphuric acid will satisfy, calculate the excess to sodium carbonate. Should there be more than enough sulphuric acid to combine with sodium and potassium, combine the excess first with calcium, as calcium sulphate, and any further excess with magnesium as magnesium sulphate. If the water contains a large amount of chlorine (more than enough to satisfy the sodium), and not enough sulphuric acid to satisfy the potassium, combine the excess of potassium with chlorine,

and if there be any chlorine still left, combine it first with magnesium, and then, if there be more than enough to saturate the magnesium, combine the excess with calcium. Calculate all calcium and magnesium not combined with chlorine and sulphuric acid to carbonates.

The following table may be found of use in the analysis of mineral and potable waters for the calculation of the number of grains in the U. S. gallon of 231 cubic inches, the number of milligrammes per litre having been found. The number of grains in the gallon has been taken as 58,318, which is believed to be the most correct figure, though authorities on the subject differ slightly from one another, *e. g.*, the U. S. Dispensatory gives 58,328.886, or nearly 11 grains more. Either of these results gives about 133.3 avoirdupois ounces in the gallon.

*Table showing the number of grains in the U. S. gallon of 231 cubic inches, corresponding to the number of milligrammes in one litre, by E. Waller, A. M., E.M.*

MGS. TO 1 LITRE = GRS. TO U. S. GAL.	MGS. TO 1 LITRE = GRS. TO U. S. GAL.	MGS. TO 1 LITRE = GRS. TO U. S. GAL.	MGS. TO 1 LITRE = GRS. TO U. S. GAL.
1...0.058318	26...1.516268	51...2.974218	76...4.493168
2...0.116636	27...1.574586	52...3.032536	77...4.490486
3...0.174954	28...1.632904	53...3.090854	78...4.548804
4...0.233272	29...1.691222	54...3.149172	79...4.607122
5...0.291590	30...1.749540	55...3.207490	80...4.665440
6...0.349908	31...1.807858	56...3.265808	81...4.723758
7...0.408226	32...1.866176	57...3.324126	82...4.782076
8...0.466544	33...1.924494	58...3.382444	83...4.840394
9...0.524862	34...1.982812	59...3.440762	84...4.898712
10...0.583180	35...2.041130	60...3.499080	85...4.957030
11...0.641498	36...2.099448	61...3.557398	86...5.015348
12...0.699816	37...2.157766	62...3.615716	87...5.073666
13...0.758134	38...2.216084	63...3.674034	88...5.131984
14...0.816452	39...2.274402	64...3.732352	89...5.190302
15...0.874770	40...2.332720	65...3.790670	90...5.248620
16...0.933088	41...2.391038	66...3.848988	91...5.306938
17...0.991406	42...2.449356	67...3.907306	92...5.365256
18...1.049724	43...2.507674	68...3.965624	93...5.423574
19...1.108042	44...2.565992	69...4.023942	94...5.481892
20...1.166360	45...2.624310	70...4.082260	95...5.540210
21...1.224678	46...2.682628	71...4.140578	96...5.598528
22...1.282996	47...2.740946	72...4.198896	97...5.656846
23...1.341314	48...2.799264	73...4.257214	98...5.715164
24...1.399632	49...2.857582	74...4.315532	99...5.773482
25...1.457950	50...2.915900	75...4.373850	100...5.831800

## CHAPTER XXXI.

### MINERAL WATER.

The term "mineral" is usually applied to water possessing medicinal properties, or an unusual amount of mineral matter. It is not proposed here to discuss the subject of mineral water, but simply to give methods of analysis of two leading varieties—alkaline carbonated water and sulphur water, that of Saratoga being an illustration of the former, and that of Chittenango, New York, an illustration of the latter. For more information on the subject, the student is referred to Fres., *Quant. Anal.*, § 206, *et seq.*, and the writers quoted by him, and also to Hunt's *Chem. and Geolog. Essays*, and his papers in *Am. Jour. Sci. and Arts*, 1865.

*Saratoga Water.*—The method given here has been followed for a long time in the Columbia College School of Mines, having originated in the private laboratory of Dr. C. F. Chandler. The constituents provided for are potash, soda, lithia, lime, magnesia, strontia, baryta, oxide of iron, oxide of manganese, alumina, chlorine, bromine, iodine, fluorine, sulphuric acid, phosphoric acid, boracic acid, carbonic acid, and silica.

*Total Solids.*—Evaporate in a weighed platinum dish from 200 to 500 c. c. of the water, on a water-bath, and dry thoroughly in an air-bath at 130° C. The weight of solid residue gives a control of the analysis. Fresenius, in his *Quant. Anal.*, § 213, says that "a more exact control is attainable as follows: By treating the residue, on evaporation, with sulphuric acid, and comparing the residue of the sulphates (the iron is present as sesquioxide) with the sum of the fixed alkalies, alkaline earths, and manganese expressed as sulphates, plus the sesquioxide of iron, the silicic acid, and the phosphoric acid (as  $\text{HPO}_3$ )."



*Oxide of Iron, Alumina, Lime, Magnesia, and Silica.*

—Acidulate 1 litre, or more, in very weak waters, with hydrochloric acid, evaporate to dryness, take up with hydrochloric acid and water, filter out the silica, and weigh it. Then determine the silica by loss, after treating with sulphuric acid and ammonium fluoride. Should there be any residue, fuse it with a little sodium carbonate, digest with water, filter out and wash the residue insoluble in water, dissolve it in hydrochloric acid, and examine the solution with the spectroscope. Should baryta or strontia be present in appreciable quantity, determine them. The residue will probably be only ferric oxide, which is to be brought into solution, and added to the filtrate from the silica. Treat the filtrate with ammonia, filter out the precipitate of ferric oxide and alumina, dissolve it in hydrochloric acid, and reprecipitate with ammonia, and determine the ferric oxide and alumina together. In the filtrates, determine the lime and magnesia, as in the analysis of limestone.

*Sulphuric Acid.*—Acidulate 1 litre of the water with hydrochloric acid, evaporate to small volume in a porcelain dish, and determine the sulphuric acid as in analysis of magnesium sulphate.

*Sodium Carbonate.*—Evaporate 1 litre of the water to dryness, digest the residue with boiling water, filter, and wash until the washings give no alkaline reaction with litmus paper. Carbonates of sodium and lithium go into solution. To the filtrate add, in slight excess, a mixture of calcium chloride and ammonia (prepared by dissolving 60 gms. of calcium chloride in 250 c. c. of water, adding to the solution 100 c. c. of ammonia, filtering, adding 100 c. c. more ammonia, and diluting to 500 c. c.). Reaction will take place between the calcium chloride and the carbonates of sodium and lithium in the water, by which calcium carbonate will be precipitated, and the chlorine unite with the sodium and lithium. Filter out the calcium carbonate, and wash it repeatedly with water

until the chlorides are removed. Then dissolve the precipitate through the filter with hydrochloric acid, precipitate the calcium as oxalate, and determine it as sulphate, as in analysis of calcite. Estimate the corresponding amount of acid sodium carbonate.

As this method of analysis, intended strictly to meet the case of Saratoga water, is applicable in most points to the analysis of other alkaline carbonated waters, it is proper to mention that in some cases it must be modified. Sodium carbonate may exist in presence of excess of carbonic acid and of magnesium carbonate, before evaporating the water, but by evaporating, calcium carbonate, magnesium sulphate and sodium sulphate will be formed. (Hunt.) In such a case it is better to determine the alkalies in excess over what is required to combine with chlorine and sulphuric acid, and calculate the sodium carbonate. In such cases, determine the sodium, as directed in analysis of fresh water.

*Potash.*—Evaporate 1 litre of the water nearly to dryness in a silver or platinum dish, filter, and wash with boiling water until the washings give no alkaline reaction with litmus. If the water is strongly saline, evaporate one tenth of the solution, on a water-bath, to the consistency of syrup, after acidulating with hydrochloric acid, and adding an amount of solution of platinum tetrachloride containing platinum tetrachloride equal in weight to four times that of the chlorides of the alkalies present, and determine the potash as directed in the analysis of potassium alum.

Should there be any sodium salt unconverted, or sodium platino-chloride difficult to dissolve in the alcohol, filter, wash on the filter with hot water, into another beaker, until only yellow potassium platino-chloride is left, evaporate the filtrate as before, after adding more platinum tetrachloride, filter, and combine the precipitates of pure potassium platino-chloride, and determine the potassium.

In water containing soluble salts of calcium, partic-

ularly calcium sulphate, some may remain with the platinum-chloride undissolved by the alcohol, and be found with the spongy platinum after ignition. In such a case, the residual platinum may be purified by boiling it with hydrochloric acid and water, filtering, and washing thoroughly. The better plan, however, in the case of water of such a character, is to determine the potassium as in the analysis of feldspar.

*Chlorine.*—Determine the chlorine in 25 c. c. of the water, after diluting it with about 100 c. c. of distilled water, by a standard solution of silver nitrate, as directed in the analysis of fresh water. In water containing less chlorine than those of Saratoga, a larger amount must be used for the determination, evaporating, if necessary. The chlorine may be determined gravimetrically, as in the analysis of barium chloride. It must be borne in mind that iodine and bromine act similarly to chlorine on the silver solution, and that a proper correction must be made on account of their presence.

*Carbonic Acid.*—Introduce into each of several bottles, of a capacity of about 300 c. c., and provided with tightly fitting glass-stoppers, exactly 50 c. c. of a solution of calcium chloride and ammonia, prepared as directed in the paragraph on sodium carbonate, and introduce into each one 200 c. c. of the water, at the spring, before the free carbonic acid has had time to escape, insert the stoppers slightly greased with pure tallow, and secure them with pieces of cloth firmly tied to the necks of the bottles. Afterward, in the laboratory, remove the stopper from a bottle, cleanse it, as well as the neck of the bottle, from all grease, drop it again loosely into the neck, place the bottle in water, and boil until violent effervescence ceases. Then filter out the calcium carbonate, rinse the bottle thoroughly with water, pouring the washings on the same filter, and keep the bottle for further treatment. Wash the calcium carbonate on the filter as long as the wash-water gives any reaction with ammonium oxalate. This

washing should be done rapidly, to avoid the formation of calcium carbonate by the carbonic acid in the atmosphere. Dissolve the calcium carbonate adhering to the bottle with a little hydrochloric acid, and wash into a beaker. Then perforate the filter with a rod, wash the precipitate through it into the same beaker, cleansing the filter with hydrochloric acid, boil, to expel free carbonic acid, determine the calcium as in analysis of calcite, and calculate the carbonic acid. Confirm the results by treating another bottle in the same way.

*Treatment for Substances in Minute Quantities.*—If the water is not alkaline to litmus without boiling, it is better to add sodium carbonate until the water has a slight alkaline reaction, as otherwise iodine and bromine may be lost by evaporation. Evaporate from 10 to 20 gallons of the water to dryness in an even number of porcelain dishes, introducing the same quantity of water into each, by which means the weighing and dividing the salts soluble in water may be avoided, as will be seen later. Complete dryness is not necessary. Treat the residues with hot water, boil, decant through two filters, repeat the treatment several times, and finally throw the residues on the filters, and wash until no trace of lithium can be detected. If it is found to be difficult to wash out the lithium from the residues, it is well to wash moderately, until no bromine can be detected in the washings, and determine the lithium in the residues.

There will be—1st. Two Insoluble Residues. 2d. Two Solutions.

*Treatment of the Insoluble Residues.*

*First Case.*—If lithium be not present in the water, or be completely removed by hot water, dissolve the residues in hydrochloric acid, combine the solutions, evaporate to dryness, add a little hydrochloric acid to the dry mass, heat, dilute with water, and filter out the residual silica, which may contain sulphates of barium and strontium. Expel the silica with ammonium fluoride and sulphuric

acid, fuse the residue with sodium carbonate, digest with water, throw the mass on a filter, wash out alkaline sulphates, dissolve the carbonates left on the filter with hydrochloric acid, and determine the barium and strontium in the manner directed later. Divide the filtrate from the silica into 3 equal parts.

*First, for phosphoric acid.*

*Second, for iron and manganese.*

*Third, for barium and strontium.*

*Treatment of the Part for Phosphoric Acid.*—Expel the hydrochloric acid, and convert chlorides into nitrates by evaporation with excess of nitric acid, diluting, adding ammonium molybdate, and proceeding as directed in analysis of iron ore.

*Treatment of the Part for Iron and Manganese.*—Precipitate the iron as basic acetate, filter, dissolve the precipitate with hydrochloric acid, and precipitate again, filter, wash with hot water, combine the filtrates, evaporate to small volume, and determine the small amount of manganese, frequently found in water as manganous oxide, as directed in analysis of manganese ore. Bring the basic acetate in sulphuric acid solution, and determine the iron by titration with solution of potassium permanganate, as in analysis of ammonio-ferric sulphate.

*Treatment of the Part for Barium and Strontium.*—Dilute the solution with water, add dilute sulphuric acid, and boil. Enough acid should be added to precipitate a little calcium, or some strontium may remain in solution. At the same time care must be taken not to precipitate too much calcium, or it will be difficult to wash, and strontium may be lost in the alcohol, which is rarely, if ever, absolute. The precipitate consisting of sulphates of barium strontium and calcium should be treated with a strong solution of ammonium carbonate, which will convert the oxides of calcium and strontium into carbonates, while the barium sulphate will be unaffected. The carbonates are then dissolved away from the barium sulphate on the

filter, with cold dilute hydrochloric acid, the barium sulphate washed with water, dried, ignited, and weighed, and the barium calculated. (H. Rose, *Pogg. Annal.*, XCV., 286, quoted by Fres., *Quant. Anal.*, § 154, 3, p. 347.) The hydrochloric acid solution is evaporated to dryness with excess of nitric acid, to convert the chlorides into nitrates, and the nitrate of calcium dissolved out with a mixture of equal parts of alcohol and ether. (H. Rose, p. 95.)

The residual strontium nitrate is dissolved in water, and the strontium determined as sulphate. (See Fres., *Quant. Anal.*, § 72, p. 107.) All the precipitates should be tested by the spectroscope.

*Second Case.*—If lithium be present, and be not completely removed by hot water, which will be almost always the case if there be much in the water, divide the hydrochloric acid solution of the residues insoluble in hot water, into 4 equal parts (instead of 3), in one of which the lithium is to be determined, while the other 3 are to be treated as directed in the *first case*.

For the determination of the lithium, evaporate the solution to dryness on a water-bath, transfer the residue to a flask, and proceed as directed later for the determination of lithium in the water solution. Also consult Fres., *Quant. Anal.*, § 209, 7, 4th London Ed., 1865.

*Treatment of Water Solutions.*—There will be two, if the plan suggested before, of evaporating the water in separate portions has been followed. Evaporate each to dryness, and appropriate one to the determination of lithium, and the other to the determination of iodine and bromine. It is to be remembered that in waters containing a large amount of chlorine, and also barium and strontium, the latter, or at least a portion, may be found in the water solution, instead of the insoluble residue, and that in such a case, a portion of the water solution must be taken for their determination.

*Lithium and Boracic Acid.*—When the solution in

which the lithium is to be determined has been evaporated to very small volume, pour about 1 c. c. of it into a watch-glass, acidulate it with hydrochloric acid, and test it with turmeric paper for boracic acid, traces of which are generally found in water of Saratoga. Wash back the fluid used for the test, and continue the evaporation to dryness. Then moisten the dry residue with hydrochloric acid, evaporate again to dryness on a water-bath; dry heat must not be used, as the lithium chloride is very easily decomposed by heat, being converted into oxide which is insoluble in absolute alcohol. After evaporating the excess of hydrochloric acid, transfer the dry residue to a capacious flask, agitate well with absolute alcohol, decant through a filter, repeat until the residue gives no reaction for lithium in the spectroscope, evaporate the alcohol on a water-bath, and dissolve the residue in water.

As magnesium carbonate is not entirely insoluble in water in presence of chlorides, some magnesium will be found in the solution resulting from the treatment of the residue of the original evaporation, and must be removed before determining the lithium as phosphate. To effect the removal of magnesium, make the solution alkaline with the barium hydrate, filter, and from the filtrate precipitate the excess of barium with ammonium carbonate, add to the filtrate about 6 gms. of pure hydro-disodium phosphate, enough pure sodium hydrate to keep the reaction alkaline, and evaporate the mixture to dryness; pour water over the residue in sufficient quantity to dissolve the soluble salts with the aid of a gentle heat, add an equal volume of ammonia, digest at a gentle heat, filter after 12 hours, and wash the precipitate with a mixture of equal volumes of water and ammonia. Evaporate the filtrate and first washings to dryness, and treat the residue in the same way as before. If some more lithium phosphate is thereby obtained, add this to the principal quantity. (See Fres., *Quant. Anal.*, § 100, p. 164.)

*Iodine, Bromine, and Nitric Acid.*—Evaporate the solu-

tion, in which these are to be determined, to dryness, transfer the dry residue to a capacious flask, and boil on a water-bath repeatedly, with 85 per cent alcohol, decanting on a filter each time, until the residue gives no reaction for bromine, when treated with fuming nitric acid and carbon disulphide. Evaporate the alcohol on a water-bath, and when the alcohol is expelled, test a little of the substance for nitric acid. To determine nitric acid, evaporate a separate portion of the water, and proceed as directed in the analysis of fresh water. After expelling the alcohol, wash the residue into a platinum dish, add about 5 times its weight of sodium carbonate, dry, and fuse. This is done to decompose any organic matter which may be present, either from having been held in the water originally or extracted from the vessels in which the water was collected. Organic matter must be removed, or it will, upon the addition of palladium chloride, cause a precipitate of palladium oxide with the iodide, and thereby vitiate the determination. Dissolve the fused mass in water, acidulate slightly with hydrochloric acid, add slight excess of palladium chloride, allow the whole to stand for 24 hours in a warm place, filter out the palladium iodide, wash with warm water, dry, ignite, and from the metallic palladium calculate the iodine.

To the filtrate from the palladium iodide add sodium carbonate in excess, evaporate to dryness, digest the dry residue with boiling absolute alcohol, decanting on a filter, and repeating the treatment until the residue gives no reaction for bromine, when tested with fuming nitric acid and carbon disulphide. When the bromine is all extracted from the residue, evaporate the alcoholic solution to dryness, after adding a little sodium hydrate, dissolve the dry residue in water, add excess of silver nitrate, filter out the precipitate of bromide and chloride of silver, wash with hot water, dry the precipitate, fuse it in a weighed porcelain crucible, and weigh. Then pour water on the fused mass in the crucible, add a little hydrochloric



acid and a fragment of zinc. In 24 hours, the silver will be completely reduced. The silver is then rubbed to powder, boiled with water containing a little hydrochloric acid, washed with pure water, gently ignited, and weighed. The difference between the atomic weights of chlorine and bromine is to the atomic weight of bromine as the difference between the amount of chloride and bromide of silver employed, and the amount of chloride which the reduced silver ought to yield is to the amount of bromine present. (See Wöhler's *Mineral Analysis*, p. 213; and Fres., *Quant. Anal.*, § 169, p. 412.)

As silver chloride is not absolutely insoluble in hydrochloric acid, it is well to test the fluid, after treating the reduced silver with hydrochloric acid to remove any traces of zinc remaining with the silver, and if any silver chloride be recovered, add the weight of it to that calculated from the reduced silver, before making the calculation as directed above. On the other hand, as a slight amount of chloride may escape reduction, it is well to treat the reduced silver with a little ammonia, filter, wash, ignite, and weigh the silver again. The loss will be silver chloride. Estimate the chlorine in it, and subtract it from the first weight. After making these corrections, calculate the bromine.

*Calculation of the Analysis.*—The sulphuric acid is combined with potassium to form sulphate.

The potassium unsatisfied by sulphuric acid is combined with chlorine to form potassium chloride.

The chlorine not required by potassium is combined with sodium to form sodium chloride.

The bromine, iodine, phosphoric acid, boracic acid, and nitric acid are combined with sodium, to form bromide, iodide, phosphate, baborate, and nitrate.

The sodium bicarbonate is determined directly.

The sodium is not determined, but is assumed as the sum of all required to combine with chlorine, bromine, iodine, phosphoric acid, boracic acid, nitric acid, and carbonic acid.

The lithium, magnesium, calcium, less that for fluorine,

strontium, barium, iron, and manganese, are combined with carbonic acid to form bicarbonate.

The fluorine is calculated to calcium fluoride.

The alumina, silica, and organic matter are reported as such.

*Sulphur Waters.*—The constituents of these waters are very similar to those found in most spring waters, with the exception of the sulphur compounds, as will be seen by the subjoined report of analyses of the waters of Chittenango, Madison Co., N. Y., taken from a lecture of Dr. C. F. Chandler, published in *Am. Chem.*, December, 1871.

## ANALYSIS OF SULPHUR WATERS.

IN ONE U. S. GALLON OF 231 CUBIC INCHES.	CHITTENANGO, MADISON COUNTY, N. Y.			
	White Sulphur Sp'g.	Cave Spring.	Magnesia Sp'ing.	Florida Spring, Montgomery Co., N. Y.
	Grains.	Grains.	Grains.	Grains.
Hydrosulphate of sodium, NaHS.....	0.117	0.316	0.757	2.008
Hydrosulphate of calcium Ca (HS) <sub>2</sub> .....	....	1.123	0.929	....
Sulphate of potassa.....	....	....	....	1.390
Sulphate of soda.....	0.213	....	....	....
Sulphate of lime.....	81.420	106.126	115.085	....
Sulphate of strontia.....	Trace.	Trace.	Trace.	....
Sulphate of magnesia.....	1.953	7.589	12.718	....
Hyposulphite of soda.....	....	0.257	0.020	0.711
Bicarbonate of soda, NaHCO <sub>3</sub> .....	....	....	....	22.143
Bicarbonate of lime.....	....	....	....	8.317
Bicarbonate of magnesia.....	22.017	23.973	20.779	6.972
Bicarbonate of iron.....	0.078	0.156	0.325	....
Chloride of potassium.....	0.156	0.233	0.333	....
Chloride of sodium.....	1.037	1.569	1.833	5.880
Chloride of lithium.....	Trace.	Trace.	Trace.	....
Alumina.....	0.082	0.222	Trace.	Trace.
Silica.....	0.286	0.519	0.577	0.798
Sulphur (in suspension).....	Trace.	....	....	....
Sulphide of iron (in suspension).....	....	....	....	0.176
Total solid contents per gallon	107.359	142.113	153.856	43.800
Total sulphur in the metallic sulphides and sulphuretted hydrogen.....	0.339	1.397	2.400	1.9165
CUBIC INCHES OF GAS PER GALLON.				
Sulphuretted hydrogen gas....	0.884	2.754	5.623	3.765
Carbonic acid gas.....	20.480	15.934	19.456	32.169

THE

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Sol

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Chlor  
Brom  
Iodide  
Fluor  
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Bicar  
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Bicar  
Bicar  
Sulph  
Phos  
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Alum  
Silica  
Orga

Total

Carbo  
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Lithi  
Lime  
Stron  
Baryt  
Magn  
Proto  
Alum  
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"The analyses were made in the Editor's laboratory, with the assistance of W. H. Chandler and F. A. Cairns."

The evaporation of large quantities of the water, and the determinations of the ordinary constituents are made in the way directed in analysis of Saratoga water.

*Sulphur Compounds.*—The following extract from the *Chem. News, American Supplement*, April, 1870, gives the method of determining the sulphur compounds: "The method employed for determining the sulphur compounds was a modification of the one employed by Simmler in the analysis of the Stachelberg water, the account of which was published in *Erdmann's Journal*, Vol. LXX. The alterations introduced lessen to a great extent the amount of analytical work to be done at the spring. The following brief statement may prove of interest:

"1. In a glass-stoppered bottle, to one litre of water was added an excess of neutral solution of nitrate of silver.

"2. To another litre was added an excess of a solution of chloride of cadmium.

"3. Through a third litre pure hydrogen was transmitted until the gas, after passing through the water, no longer decolorized a dilute solution of iodide of starch. An excess of a solution of chloride of cadmium was then added.

"These three bottles were well agitated, securely sealed, and transported to the laboratory. From each, the precipitate was filtered, washed, dissolved, and oxidized by fuming nitric acid and potassium chlorate, filtered, and the sulphuric acid determined in the filtrate with barium chloride.

"No. 1. This precipitate contained the sulphur, existing in the form of sulphides and hyposulphites.

"No. 2. Contained the sulphur existing in the form of sulphides, including the free sulphuretted hydrogen.

"No. 3. Contained the sulphur present in the form of sulphuretted sulphides. The difference between No. 3 and No. 2 indicated the amount of sulphur as free sul-

phuretted hydrogen ; and by deducting No. 2 from No. 1, the amount of hyposulphites was ascertained.

“In the original filtrate from No. 1, the sulphuric acid was determined, after removing the excess of silver by hydrochloric acid.”

The changes made in Simmler's method were suggested by Wm. H. Chandler. Bromine may be used instead of nitric acid and potassium chlorate in oxidizing the precipitates containing sulphur.

## CHAPTER XXXII.

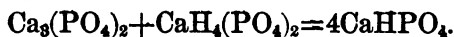
### SUPERPHOSPHATE OF LIME.

*(For Agricultural Purposes.)*

It is so called from the fact that by treatment with acid the common tri-calcium phosphate (bone phosphate) is converted, according to the quantity of acid used, into either mono-calcium, or di-calcium, phosphate. If a sufficient quantity of sulphuric acid, for instance, be used, all the calcium will be withdrawn, and only phosphoric acid be left. The treatment for the production of soluble phosphate or superphosphate is represented by the following equation :



This is theoretical, and is rarely carried out in the manufacture of fertilizers. There is usually some bone phosphate unconverted, owing to the use of an insufficient quantity of acid. Suppose some tri-calcium phosphate to remain mixed with mono-calcium phosphate, and reaction to take place between them, as represented by the following equation :



The result is a phosphate called by the names "returned," "reduced," "reverted," "precipitated." Tri-calcium or bone phosphate is insoluble in water, and di-calcium, or precipitated, very slowly soluble. Consequently, the value of the fertilizer depends chiefly upon the quantity of soluble phosphate present. The sample should be thoroughly mixed to insure that the portion taken for analysis fairly represents the average quality.

Commercial superphosphate of lime always contains more or less moisture, which may vary greatly on keeping the sample. To avoid error from this source, a portion

should be taken for the determination of moisture (by drying 1 gm. at 100° C., until it ceases to lose weight), at the same time that portions are weighed out for the determination of the other constituents. Some chemists prefer to determine the moisture on a larger portion of the sample as received (up to 10 gms. or more) and then to dry half a pound or more of the sample on the water-bath, pulverizing and mixing it as it dries, and to use portions of the sample thus dried for determination of the moisture left, and for phosphoric acid, etc. (Stillwell, *Proc. Am. Chem. Soc.*, II., 64.) The results must be calculated back so as to show the composition of the moist sample (as received).

There are two methods of determining the different phosphates present in a fertilizer usually followed by chemists, as follows :

*First Method.*—Weigh 1 gm. of the superphosphate, transfer it to a shallow mortar, rub up with 50 c. c. of warm water (of a temperature of about 60° C.), and pour the turbid fluid on a filter ; then add 50 c. c. more warm water, triturate again, and pour the water containing the finer particles of the material on the filter. Repeat this treatment with 50 c. c. more warm water, pour all the contents of the mortar on the filter, and wash with enough warm water to make the volume of fluid equal to 200 c. c. There will now be a filtrate containing the soluble phosphoric acid, and a residue containing the insoluble and precipitated phosphoric acid.

*Soluble Phosphoric Acid.*—To the filtrate containing the soluble phosphoric acid add 4 or 5 gms. of sodium nitrate, and the same quantity of sodium carbonate, evaporate to dryness, fuse to destroy the organic matter extracted by the water, the heat of an open Bunsen burner being sufficient, remove the fused mass from the crucible with hot water, boil, and filter, if necessary. As nearly all of the phosphoric acid in superphosphates is soluble, and is consequently in this solution, dilute to 1 litre, and take



200 c. c., or one fifth of it, for phosphoric acid, to be determined by means of ammonium molybdate.

The largest amount of phosphoric acid that can be present in pure bone phosphate is less than 46 per cent. As all, however, is rarely converted into soluble phosphate, and as there is usually a large amount of other substances present, it may be safely assumed that 50 c. c. of ammonium molybdate solution, 1 c. c. of which will precipitate 1.3 milligrammes of phosphoric acid, is sufficient in all cases to precipitate the soluble phosphoric acid in one fifth of a gm. of superphosphate.

*Precipitated Phosphoric Acid.*—Wash the residue containing the insoluble and precipitated phosphoric acid into a beaker, add a solution of 15 gms. of ammonium citrate in 50 c. c. of water (equivalent to sp. gr. 1.05), warm at a temperature of 60° C. for three quarters of an hour, filter and wash with about 150 c. c. of water of 60° C. Treat the filtrate as before with nitrate and carbonate of sodium (4 or 5 gms. of each), evaporate to dryness, fuse, take up with water, acidulate with nitric acid, boil, filter if necessary, and, as the amount of precipitated phosphoric acid is small, treat the whole solution with about 25 c. c. of ammonium molybdate solution, determining the phosphoric acid as usual.

*Insoluble Phosphoric Acid.*—Fuse the residue left after extracting the soluble and precipitated phosphoric acid, with sodium nitrate and carbonate (4 or 5 gms. of each), over a common Bunsen burner, remove the mass from the crucible with water and nitric acid, boil, and filter if necessary. As the amount of insoluble phosphate is small, use all the solution for determining the phosphoric acid. Add to the solution about 25 c. c. of ammonium molybdate solution, and proceed as usual.

*Second Method.*—A better method is the one adopted by a committee of German chemists and reported by Fresenius, one of the number, in the *Zeit. für Anal. Chem.*, Vol. VII., p. 304. See also *Am. Chem.*, October, 1871.

Treat 1 gm. with water alone, as directed in first method, to dissolve out the soluble phosphate, and, after drying, fuse the residue with nitrate and carbonate of sodium (about 4 or 5 gms. of each), dissolve the fused mass with water and nitric acid, and treat the whole solution for phosphoric acid, as in the first method, with ammonium molybdate. This will give the *insoluble and precipitated phosphoric acid*. At the same time, treat another gm. with water and ammonium citrate, as in the first method, to remove the soluble and precipitated phosphoric acid, and fuse the dried residue as before. As the *insoluble phosphoric acid* is small in amount, determine it in the whole solution as before.

At the same time that the two portions are being treated for insoluble phosphoric acid, and for insoluble and precipitated phosphoric acid (together), fuse another gm. of the superphosphate with nitrate and carbonate of sodium (5 gms. of each), bring into solution with water and nitric acid as before, dilute to 1 litre, and in 200 c. c., equivalent to one fifth of a gm., determine the total phosphoric acid.

By deducting, from the amount of total, the amount of insoluble and precipitated, that of soluble phosphoric acid is estimated.

By deducting, from the amount of insoluble and precipitated, that of insoluble, the amount of precipitated phosphoric acid is estimated.

In cases where iron and aluminum are not present, phosphoric acid may be determined volumetrically, by means of uranium, with sufficient accuracy for determining the value of superphosphate for fertilizing purposes.

*Solutions Required.*—A solution of *uranium acetate*, prepared by dissolving about 34 gms. in 1 litre of water.

A solution of 10.085 gms. of pure *crystallized hydrodisodium phosphate* in 1 litre of water. The salt should be uneffloresced, coarsely powdered, and dried by pressing between folds of bibulous paper before weighing.

A solution of *sodium acetate*, prepared by dissolving 100 gms. of sodium acetate in water, adding 100 c. c. of acetic acid, and diluting to 1 litre.

A solution of *potassium ferrocyanide*.

*Uranium Solution*.—This is standardized by means of the sodium phosphate solution, of which 50 c. c. are introduced into a beaker, and heated to about 100° C. on a water-bath.

After adding 5 c. c. of the sodium acetate solution, the uranium solution is run in from a burette, rapidly up to the amount of 15 c. c., and then, drop by drop (testing frequently by placing a drop of the sodium phosphate solution on a white porcelain plate and adding a drop of the potassium ferrocyanide solution). As soon as the uranium is in excess, a reddish-brown coloration appears. The solution is then heated on a water-bath for a few minutes, and the test repeated. If the same reaction takes place, the titration is completed. The uranium solution should be of such a strength that 20 c. c. of it are equal to the 50 c. c. of phosphate solution. If this should not be the case, as the uranium solution is purposely made too strong, dilute accordingly, and repeat the titration on another portion of the phosphate solution, to insure correctness.

*Analysis*.—This is made under conditions as nearly similar as possible to those under which the standardizing was performed. Add to the fluid to be examined, 5 c. c. of the sodium acetate solution, and proceed with the titration in the manner directed for standardizing the uranium solution.

As 1 c. c. of the uranium solution is equivalent to 0.005 gm. of phosphoric acid, the calculation of the amount in the solution under examination is very simple.

*Chlorine*.—Digest 1 gm. with about 50 c. c. of water, filter, wash, make the filtrate alkaline with sodium carbonate, add a little sodium nitrate, evaporate to dryness, fuse gently, take up with water, and determine the chlorine volumetrically with standard silver nitrate solution.

*Sulphuric Acid.*—Make a solution of 1 gm. as for chlorine, acidulate with hydrochloric acid, and determine the sulphuric acid with barium chloride, as usual.

*Free Sulphuric Acid.*—Make an aqueous solution of the superphosphate (1 or 2 gms.), evaporate slowly, until only a small quantity is left; add about 7 volumes of absolute alcohol, and allow to settle in the cold for some hours. This precipitates all sulphates, and leaves in solution, besides phosphates, the free sulphuric acid. Filter, wash with alcohol, add a large amount of water to the solution, carefully evaporate off the spirit, and estimate the acid in the solution in the usual manner by precipitation with barium chloride. (Crookes's *Select Methods*, p. 312.)

*Moisture.*—Dry 1 gm. to constant weight at a temperature of 100° C.

*Ammonia.*—See analysis of guano.

*Alkalies.*—Make a water solution of 2 or 3 gms. of the superphosphate, and determine the alkalies as in the analysis of water.

*Ash.*—Incinerate 4 or 5 gms. of the superphosphate until all carbonaceous matter is consumed, cool, and weigh. If the ash is not of a light color, and free from all black specks, repeat the ignition and weighing.

For a method of making an exhaustive analysis of superphosphate, consult Fres., *Quant. Anal.*, § 235.

## REPORT.

Soluble phosphoric acid.....	.....
Precipitated phosphoric acid.....	.....
Total available phosphoric acid ( $P_2O_5$ )*.....	.....
Equivalent to bone phosphate [ $Ca_3(PO_4)_2$ ]*.....	.....
Insoluble phosphoric acid.....	.....
Equivalent to bone phosphate.....	.....
Total phosphoric acid.....	.....
Equivalent to bone phosphate.....	.....
Nitrogen.....	.....
Equivalent to ammonia ( $NH_3$ ).....	.....
Potash ( $K_2O$ )....	.....
Equivalent to potassium sulphate ( $K_2SO_4$ ).....	.....
Soda ( $Na_2O$ ).....	.....
Equivalent to sodium sulphate ( $Na_2SO_4$ ).....	.....
Water.....	.....

\*1 gm.  $P_2O_5$  is equivalent to 2.1881 gms.  $Ca_3(PO_4)_2$ , as will be found by stoichiometrical calculation. The factor is a convenient one to use in calculating results in this analysis or in that of guano.

## CHAPTER XXXIII.

### MILK.

The constituents are water, sugar, casein, and ash or mineral salts.

Weigh a small platinum dish; then add a 5-gm. weight to those on the pan, and run in from a pipette enough milk to weigh a few milligrammes over 5 gms., determine the exact weight as quickly as possible and proceed.

*Water.*—Evaporate over a water-bath, until the milk solids look dry; then dry in an air-bath at 100° to 105° C. for one to one and a half hours, weigh, and dry again, for one half to three quarters of an hour, and weigh again. Repeat this treatment until the loss is less than 5 milligrammes.

Long heating should be avoided, as far as possible, as the sugar is apt to decompose and affect the results.

*Fat.*—Weigh a small beaker and have ready a water-bath full of boiling water. Pour about 10 c. c. of ether on the milk solids, allow it to soak into the solids for a few minutes, place the dish on the water-bath, and keep it there until the ether boils. Then, after drying the bottom of the dish with bibulous paper, pour the ether into the weighed beaker, by means of a glass rod. If the milk solids flake off from the dish and become stirred up in the ether, a little care will suffice to prevent their being carried over into the beaker, as they sink rapidly in the ether. Repeat this treatment with ether about 6 times. Cover the beaker with a piece of filter-paper, and evaporate off the ether over hot water, being careful to have no flame near the beaker. When the ether is all gone, dry the beaker in an air-bath at 100° to 105° C., for about 15 minutes. The residue is *butter-fat*. Should it contain any water, this should be driven off at as low a tempera-

ture as possible, that is, on a water-bath rather than in an air-bath. The milk solids, after treatment with ether, require about 30 minutes' drying at 100° to 105° C. after the ether is all gone. When water is present, the direct determination gives results a little low, as the expulsion of the water appears to cause some decomposition of the butter, making the color dark, and giving it a peculiar odor. The determination by direct weight of the butter and that by loss seldom agree exactly, but usually within 5 milligrammes or less.

*Sugar.*—After extracting the butter and expelling the ether, nearly fill the dish with water, place it on a boiling-water bath, leave it there for about 20 minutes, pour off the water into a previously weighed dish of similar size, and place this also on a water-bath to evaporate. Repeat this treatment with water 4 or 5 times. After the contents of the dishes appear dry, leave them in an air-bath, heated to 100° C., for about 2 hours, cool, and weigh them. If the loss and direct weight agree, further drying is unnecessary; otherwise, dry and weigh again. This gives the sugar and some soluble mineral salts.

*Ash of Sugar.*—Ignite the dish containing the sugar at as low a temperature as possible, to avoid the loss of salts volatile at high temperature, such as potassium chloride, etc. The residue is the ash of sugar, and the loss by ignition, sugar.

*Casein.*—After extracting the sugar, the residue left in the dish is casein, and some insoluble mineral salts.

*Ash of Casein.*—Ignite the dish containing the casein, cool, and weigh. The residue will be ash of casein, and the loss by ignition casein.

*Ash or Mineral Salts.*—Combine the weights of ash of sugar and ash of casein. The sum will be the ash or mineral salts.

For most purposes, the determination of water and butter is sufficient, giving water, butter, and solids, not fat.

The British Society of Public Analysts fixes on maximum water as 88.5 per cent, and minimum butter as 2.5 per cent, and solids, not fat, as 9 per cent. (*Chem. News*, XXXI., p. 58, 1875.)



### Formula of Normal Solution

$S$  = Substance

$w$  = Molecular weight of Substance

$Z$  = Solution

1 cc. of  $Z$  must contain  $w$  (m. grams) of  $S$

## CHAPTER XXXIV.

### ACIDIMETRY AND ALKALIMETRY.

The solutions usually employed are of sulphuric acid, hydrochloric acid, oxalic acid, sodium or potassium hydrate, and also of some substance which is colored differently by acids and alkalies, such as litmus, cochineal, coralline, logwood, etc.

A solution is styled normal when the molecular weight of the substance is the same as the number of milligrammes of it in 1 c. c. of the solution.

*Half-Normal Sulphuric Acid.*—This solution is prepared so as to contain 0.049 gm.  $H_2SO_4$ , or 0.040 gm.  $SO_3$ , in each c. c. To 600 c. c. of water add about 20 c. c. of chemically pure concentrated sulphuric acid, mix well, and allow to cool. Measure out from the burette two portions of exactly 20 c. c., add to each portion 50 c. c. of hot water, and 40 c. c. of a saturated solution of barium chloride. Treat the precipitates of barium sulphate, and determine the sulphuric acid. If the precipitates do not differ in weight more than 0.010 gm., take the average, calculate the sulphuric acid in 1 c. c. of the solution and dilute, as directed afterward.

Another method is as follows :

Introduce about 3 gms. of dry C. P. sodium carbonate into a weighed platinum dish, heat to  $180^{\circ}C$ , or just below redness, for a few minutes, cool, and weigh, repeating to constant weight. This gives the weight of the sodium carbonate. Then add to the contents of the dish about 30 c. c. of water, warm until the sodium carbonate is dissolved, run in from a burette 20 c. c. of the sulphuric acid solution, keeping the dish covered while doing so, heat on a water-bath, with the cover on, until all free carbonic acid is expelled ; then remove the cover, after washing it and

allowing the washings to run into the dish, continue the evaporation to perfect dryness, heat, as in the first instance, to constant weight, either in an air-bath at  $180^{\circ}$  C., which is the better plan, or over an open flame, at a heat just below redness. The increase in weight is proportional to the amount of sulphuric acid used, so long as there is an excess of sodium carbonate over acid.

The calculation of the value of the solution is made by the following proportion: The difference between the molecular weights of sulphuric acid and carbonic acid (36) is to the molecular weight of sulphuric acid (98) as the difference in the weights of dish and contents, before and after adding sulphuric acid, is to the weight of sulphuric acid used, and as 20 c. c. of sulphuric acid were used, this result divided by 20 will give the value of 1 c. c. of the acid.

It is customary to calculate the result in terms of  $\text{SO}_2$  instead of  $\text{H}_2\text{SO}_4$ . Suppose it is found by the experiment, that 1 c. c. of the solution contains 0.044 gm. of  $\text{SO}_2$  instead of 0.040 gm., and, consequently, 100 c. c. contain 4.400 gms. instead of 4 gms., then as 4 gms. are to 100 c. c. so are 4.4 gms. to 110 c. c. Therefore, 10 c. c. of water must be added to each 100 c. c. of the acid solution. To do this, fill a dry 500 c. c. flask to the holding mark with the acid solution, pour it into a clean dry bottle, introduce into the flask 50 c. c. of water, and pour this also into the bottle, after shaking well, pour the fluid back into the flask, and finally into the bottle for use. This is done to mix the fluid thoroughly. The bottle should be kept corked. This is what is called half-normal sulphuric acid solution, 1 c. c. of which contains 49 milligrammes of  $\text{H}_2\text{SO}_4$ , or 40 milligrammes of  $\text{SO}_2$ .

A solution of sodium carbonate may be used to obtain the solution of half normal sulphuric acid, thus: Heat a moderate amount of pure dry sodium carbonate in a platinum dish, until it begins to sinter together. Transfer, while hot, to a dry specimen tube or flask; cork it up and

allow the salt to cool out of contact with the air. With this material make a half normal solution (53 grammes in 1 litre, or 26.5 grammes in 500 c. c., etc.). Mix the solution well and place some in a burette. Do the same for the sulphuric acid solution made as first described. Run 10 c. c. of the sodium carbonate solution into a beaker, add to it 10 c. c. of the sulphuric acid, or enough to render it acid, and boil to expel the carbon dioxide, which would otherwise affect the indicator and thus interfere. Then add a few drops of the indicator (cochineal is preferable in this case) and run in the sodium carbonate solution until the color shows that the solution is neutral. From the data thus obtained, calculate the amount of dilution required for the sulphuric acid; *e. g.*, suppose 10 c. c. sodium carbonate solution were used at first—then 10 c. c. sulphuric acid, and finally, after boiling, 2.3 c. c. sodium carbonate to effect neutrality, as shown by the color imparted by the indicator. Then 10 c. c. of the sulphuric acid neutralizes  $(10 + 2.3)$  12.3 c. c. sodium carbonate solution. But the sulphuric acid should be half normal, or neutralize the sodium carbonate c. c. for c. c. Therefore 12.3 c. c. sulphuric acid ought to have been used if the solution was of the right strength; or, every 100 c. c. of the acid solution should be diluted to 123 c. c.

Measure the amount of the diluted acid on hand, dilute in the proportion indicated, rinse out the burette, mix well, and repeat the test in the same way, diluting again if necessary, until the solutions correspond exactly. The accuracy of the sulphuric acid solution should finally be verified gravimetrically by precipitation with barium chloride solution, etc.

*Normal Potassium Hydrate.*—This solution is prepared so as to contain 0.0561 gm. of potassium hydrate, (KHO) or 0.0471 gm. of potassium oxide ( $K_2O$ .)

Dissolve about 20 gms. of potassium hydrate in 300 c. c. of water, and when dissolved fill a Mohr burette with the

solution to the zero mark, and run it, drop by drop, into a beaker containing 10 c. c. of the standardized sulphuric acid diluted to 200 c. c., and also a little cochineal solution. Continue to add the alkaline solution until the yellow color, which is the color produced upon cochineal by acid, becomes carmine, showing that the fluid has become alkaline. Repeat upon different quantities of acid. The color imparted to any number of c. c. of the sulphuric acid solution, by the cochineal, should change upon the addition of exactly the same quantity of alkaline solution. If it does not, the potassium hydrate solution must be diluted until the two solutions agree. Suppose it is found by experiment that 10 c. c. of the acid solution requires only 8 c. c. of the alkaline, then, to every 8 c. c., 2 c. c. of water must be added, or to each 100 c. c. of solution 25 c. c. of water. Employ the same method of diluting and mixing as in the case of standard sulphuric acid. Now, if 1 c. c. of the solution of potassium hydrate exactly neutralizes 1 c. c. of the solution of sulphuric acid, the quantity of  $K_2O$  and  $SO_3$  must be exactly in proportion to their molecular weights, and as each c. c. of the acid solution was found to contain 0.040 gm. of  $SO_3$ , each c. c. of the alkaline solution must contain 0.0471 gms. of  $K_2O$ , as 80 parts of  $SO_3$  are neutralized by 94.2 parts of  $K_2O$ , or 0.040 gm. of  $SO_3$  by 0.0471 gm. of  $K_2O$ . It is sometimes convenient to use potash lye of unknown strength for the preparation of the standard alkaline solution, in which case the quantity of alkali in a given volume can be determined approximately by finding the specific gravity of the lye with a hydrometer, and calculating the per cent of alkali by reference to the table in the *Appendix*, which gives the per cent of  $K_2O$  in solutions of different specific gravities.

*Indicators.*—The coloring matters used to show when the fluid is acid or alkaline are so called. Although a great many have been prepared, only a few are in common use:

**Litmus:** To prepare this, Sutton directs to boil the litmus, reduced to coarse powder, two or three times with alcohol of about 80 per cent, and throw the liquid so obtained away. Then digest the litmus repeatedly with cold water until all soluble color is extracted, let the mixed washings settle clear, decant, and add to them a few drops of concentrated sulphuric acid until quite red, then heat to boiling; this will decompose the alkaline carbonates and convert them into sulphates. Now cautiously add baryta water until the color is restored to blue or violet, let the barium sulphate settle perfectly, and decant into a proper vessel for use. The solution must be kept in an open bottle, as it loses color in a closed vessel, although it will recover it upon exposure. Litmus cannot be used in the presence of carbonic acid; consequently, the standard alkali, if litmus is used as the indicator, must be entirely free from it.

**Cochineal:** Macerate, with frequent shaking, about 3 gms. of good cochineal (in powder) with 250 c. c. of a mixture of 3 or 4 volumes of distilled water, and 1 volume of alcohol, and filter through Swedish paper. It keeps well in closed bottles. It cannot be used in the presence of salts of iron, but is not affected by carbonic acid—at least, in moderate quantity.

**Logwood:** Boil down a few shavings from the interior of a piece of logwood with distilled water, and mix the concentrated decoction with 1 to 2 volumes of alcohol. It must be kept unexposed to light. It cannot be used in presence of oxides of the heavy metals.

**Coralline:** An alcoholic solution of this is extremely sensitive, and rapid as an indicator, and is particularly well adapted to the titration of vinegar and organic acids generally.

**Normal Hydrochloric Acid.**—Mix 500 c. c. of water with 100 c. c. of pure hydrochloric acid of 1.12 sp. gr., run out from a burette 2 portions of exactly 20 c. c. each, and determine the amount of hydrochloric acid in each, with

silver nitrate, as directed in the analysis of barium chloride. If the two results agree closely, take the mean, calculate the amount of water necessary to make the solution of such a strength that 1 c. c. will contain 0.03646 gm. of hydrochloric acid. If a normal solution of potassium hydrate is at hand, also test a portion of the solution with it. The solutions should agree.

$\text{C}_2\text{H}_2\text{O}_4 + 2\text{H}^+\text{O}$  *Half-Normal Oxalic Acid.*—Dissolve 63 gms. of pure crystallized oxalic acid in 1 litre of water and standardize the solution by titrating a portion of it with standardized potassium hydrate solution, or standardized potassium permanganate solution.

These standard solutions may be kept in well-closed bottles for some time without appreciable change. Glass-stoppered bottles should be used for the acid solutions. The bottles containing the alkaline solutions should be closed with tightly-fitting corks which have been dipped in melted paraffine.

These standard alkalimetric and acidimetric solutions find application in many of the processes of quantitative analysis, which it would be here unnecessary to specify. As samples of their application we will take the titration of crude sodium carbonate and the determination of the acidity of vinegar.

*Crude Sodium Carbonate.*—Weigh out 5.3 gms. of the sample (= one twentieth of an equivalent of  $\text{Na}_2\text{CO}_3$ ), dissolve in a little hot water, filter, and wash the residue, bringing the bulk of filtrate and washings up to 100 c. c. Thoroughly mix this solution by pouring it backward and forward a few times from the flask to the beaker. Then take 10 c. c. of the solution, run in 10 c. c. of the half-normal sulphuric acid solution, dilute with about 40 c. c. of water, boil to expel excess of carbonic acid, add a few drops of cochineal, and then run into it normal potassic hydrate solution until the solution is exactly neutral. Repeat the operation with 2 or 3 other portions of 10 c. c. each, and take the average. The number of c. c. of sul-

phuric acid solution which have been neutralized by the solution of the sample, multiplied by 10, give at once the percentage of  $\text{Na}_2\text{CO}_3$  present in the sample, since one twentieth of an equivalent of that compound was taken, and half-normal acid was used. We might have taken a round 5 gms., but in that case an unnecessary elaboration is introduced into the calculation.

This method of weighing out one tenth or one twentieth of an equivalent in gms. of a substance, dissolving to 100 c. c., and titring portions thereof, is usually the most convenient mode of procedure. In some cases, it may be convenient to make a one-twentieth normal solution of sulphuric acid, or of potassium hydrate to correspond.

For vinegar, weigh out in a stoppered flask 60 gms. of the vinegar, dilute to 1000 c. c. (or 30 gms., and dilute to 500 c. c.), mix thoroughly, and take 100 c. c. at a time for titration with the potassium hydrate solution. In this case, it is best to use coralline as an indicator, since the cochineal does not show a sufficiently marked deviation from the neutral tint, when only small amounts of free acetic acid are present. The number of c. c. of potassium hydrate solution required just to give a *full alkaline*\* color, show the percentage of acetic acid present, since in this case an equivalent of acetic acid was weighed out, the percentage of acetic acid being usually small (about 3 to 10 per cent).

In commerce, vinegars are often spoken of as "twenty grain," "thirty grain," "forty grain," etc. This means that one Troy ounce of the vinegar will exactly neutralize 20, 30, 40, etc., grains of potassium bicarbonate ( $\text{KHCO}_3$ ), and usually dealers desire to have the results expressed in this form. In such cases, it is easy to calculate, from the figures obtained, the number of grains of potassium hydrogen carbonate (bicarbonate) necessary to neutralize a Troy ounce by multiplying the percentage obtained by 8.008. The reason for employing this factor is that there are 480 grains in a Troy ounce, and the number of grains

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\* Neutral alkaline acetates have a slight alkaline reaction.

of  $\text{KHCO}_3$  necessary to neutralize 480 grains of pure acetic acid is found to be 800.8 by the following proportion :

$$(\text{HC}_2\text{H}_3\text{O}_2 : \text{KHCO}_3 =) 60 : 100.1 = 480 : 800.8.$$

The decimal place is changed two points in the factor because the figure expressing percentage is 100 times too great, being expressed as a whole number, instead of what it really is, parts in 100. Suppose, for instance, the percentage found to be 6.5 ; then  $6.5 \times 8.008 = 52.052$  grains of  $\text{KHCO}_3$  required to neutralize one Troy ounce. It is always best to verify the result by weighing out a Troy ounce (31.100 gms.), adding to it an amount of potassium hydrogen carbonate corresponding to the number of grains found (having determined the strength thereof by titration beforehand), boiling and testing the reaction of the solution, which should be just alkaline. If it is not, the test must be repeated.

On account of the strong color of some vinegars, which prevents one from seeing the change of color in the indicator, some analysts prefer to distill the acetic acid off, and obtain a clear solution for titration (*vid.* Blyth, *Manual of Practical Chem.*, p. 210.) Of course, when it is desirable to know only the weight of acid in a given bulk of solution, as number of ounces in 1 gallon, the acid may be measured out, and diluted to any convenient strength, and aliquot portions taken for titration.



## CHAPTER XXXV.

### COMMERCIAL BICARBONATE OF SODA.



*Moisture.*—Weigh out 1 gm. in a platinum boat, and place the boat and contents in the centre of a piece of hard glass tubing about 8 or 10 inches long. Connect the tubing at one end, by means of a tightly-fitting tube and cork, with a bottle containing concentrated sulphuric acid to dry the air drawn through it, and at the other end with a calcium chloride tube, previously weighed and prepared by passing  $CO_2$  through it as previously described. (Limestone, p. 59; Elementary Analysis of Sugar, p. 230.) The point of the calcium chloride tube should be passed through the cork, as a connection of rubber tubing is very likely to condense the water driven off, which is drawn into the tube then only with difficulty. The other end of the calcium chloride tube is then connected with an aspirator. Start the aspirator, and then apply the heat of a Bunsen lamp to the tubing where the boat lies. Raise the heat steadily until the tube about it is red hot. Keep it at that temperature for fifteen minutes or more. Then withdraw the heat and allow it to cool, still keeping the aspirator at work, until the tubing and calcium chloride tube are cool. Weigh the calcium chloride tube. The increase in weight is the moisture present in the sample. Withdraw the boat, and weigh it with its contents. The loss represents water plus half the carbon dioxide. This should be one half the amount of the carbon dioxide as determined afterward.

*Carbon Dioxide.*—Introduce 0.5 gm. into the flask of a carbon dioxide apparatus, and 25 c. c. water containing 2 c. c. concentrated sulphuric acid, or 5 c. c. concentrated nitric acid, and determine the  $CO_2$  as usual in carbonates,

by absorption in a tube of soda-lime, etc. (See Limestone, p. 59.)

*Hygroscopic Moisture.*—Dry 1 or 2 gms. in the air-bath at 100° C. to constant weight. The loss represents hygroscopic moisture. This, deducted from total water determined as above, gives water due to  $\text{NaHCO}_3$ . Also, from the percentage of  $\text{CO}_2$  calculate the water due to  $\text{NaHCO}_3$ . These two results should agree—



*Soda Combined as Carbonate.*—Dissolve 1 gm. in about 100 c. c. of water, add cochineal solution, and then run in from a burette an excess of standard sulphuric acid solution. (Alkalimetry, p. 207.) Boil out the carbon dioxide, and titre back with standard potash solution, and from these results calculate the amount of  $\text{Na}_2\text{O}$  combined as carbonate.

*Chloride.*—Dissolve 1 gm. in 100 c. c. of water, just neutralize with  $\text{HNO}_3$ , add a few drops of saturated solution of potassium chromate, (1 : 5) and titre with standard solution of silver nitrate. The silver nitrate solution is made by dissolving 17 gms. pure crystallized  $\text{AgNO}_3$  in one litre of water. It is standardized by testing it upon a solution of pure fused sodium chloride\* containing 1 gm. in 250 c. c. of water. The potassium chromate is used as an indicator, since the red silver chromate cannot form (permanently) until all of the chloride has been precipitated. The silver solution is, therefore, added until the liquid has a reddish tinge, which cannot be removed by vigorous stirring.

*Sulphate.*—Dissolve 3 or 4 gms. in water, acidulate slightly with hydrochloric acid, boil out the carbon dioxide, and determine  $\text{SO}_3$  as usual with  $\text{BaCl}_2$ .

Calculation: Calculate the Cl to  $\text{NaCl}$ , the  $\text{SO}_3$  to

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\* Most conveniently prepared by neutralizing pure sodium carbonate with hydrochloric acid, evaporating to dryness and fusing. All ordinary salt (table salt) contains small amounts of sulphates, chiefly calcium and magnesium, and other impurities, which cannot be separated without some trouble.—E. W.

$\text{Na}_2\text{SO}_4$ . The  $\text{Na}_2\text{O}$  found by alkalimetical titration represents that combined as carbonate—mono or bi—since the neutral  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  have no effect.

For calculating the amount of mono- and bicarbonate present let us take an example. Suppose we have found in a sample :

Total  $\text{CO}_2$ , 50.462 per cent; total  $\text{Na}_2\text{O}$ , 37.894 per cent.

First calculate the soda to  $\text{CO}_2$  for monocarbonate  $(\text{Na}_2\text{O} + \text{CO}_2 = \text{Na}_2\text{CO}_3) - A$ ;

then,  $(\text{Na}_2\text{O} : \text{CO}_2 =) 62 : 44 = 37.894 : x_1$

$$x_1 = 26.892 \text{ CO}_2.$$

By subtracting this from the total  $\text{CO}_2$  we obtain the excess of  $\text{CO}_2$  due to bicarbonate,  $50.462 - 26.892 = 23.570 \text{ CO}_2$ . This represents just half of the  $\text{CO}_2$  of the bicarbonate, since  $2\text{NaHCO}_3 = (\text{Na}_2\text{O} + \text{CO}_2) + (\text{H}_2\text{O} + \text{CO}_2) - B$ .

By doubling it, then, we get the whole amount of  $\text{CO}_2$  due to bicarbonate present in the sample.

$$2 \times 23.570 = 47.140 \text{ CO}_2.$$

Calculate this to bicarbonate :

$$(\text{CO}_2 : \text{NaHCO}_3 =) 44 : 84 = 47.140 : x_2.$$

$$x_2 = 89.995 \text{ per cent bicarbonate present.}$$

Calculate it also to  $\text{Na}_2\text{O}$ . In the formula  $B$ , given above,  $2\text{CO}_2$  balance one  $\text{Na}_2\text{O}$ ; therefore,

$$(2\text{CO}_2 : \text{Na}_2\text{O} =) 88 : 62 = 47.14 : x_3.$$

$$x_3 = 33.212 \text{ Na}_2\text{O in bicarbonate.}$$

The remainder of the  $\text{Na}_2\text{O}$  found  $(37.894 - 33.212 = 4.682)$  is present as monocarbonate.

Calculate accordingly :

$$(\text{Na}_2\text{O} : \text{Na}_2\text{CO}_3 =) 62 : 106 = 4.682 : x_4.$$

$$x_4 = 8.004 \text{ per cent of monocarbonate present.}$$

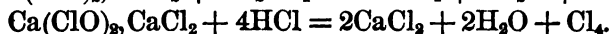
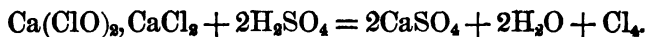
To verify the calculation :

$\text{CO}_2$ due to bicarbonate ( $x_2$ ).....	47.140 per cent.
$\text{CO}_2$ due to monocarbonate ( $x_4 - 4.682$ ).....	8.322 " "
Total $\text{CO}_2$ .....	50.462 " "

## CHAPTER XXXVI.

### CHLORIMETRY.

Bleaching powder, commercially known as chloride of lime, consists of a mixture, according to some a combination, of calcium hypochlorite,  $\text{CaCl}_2\text{O}_2$ , and calcium chloride,  $\text{CaCl}_2$ . Its value depends upon the amount of chlorine set free when an acid is added, known as "available chlorine," *e. g.* :



The available chlorine of bleaching powder is two atoms of Cl for each atom of O in the hypochlorite, or, as the formula indicates,  $\text{O}_2$  and  $\text{Cl}_4$ .

The compounds known commercially as chloride of soda (Labarraque's solution) and chloride of potash (Javelle water) are similar in composition ( $\text{NaClO}$ ,  $\text{NaCl}$ ) and ( $\text{KClO}$ ,  $\text{KCl}$ ), and are the same as regards the ratio of O and Cl.

*"Iodized Starch" Paper.*—Rub up in a mortar 3 gms. starch with 50 c. c. warm water, wash the creamy mixture into a beaker containing about 200 c. c. boiling water, stirring well until solution is effected. Now add a solution of 1 gm. KI and 1 gm. pure  $\text{Na}_2\text{CO}_3$ , and dilute to half a litre. Moisten strips of filter-paper with this solution, and dry them for use, keeping them in a corked or stoppered bottle.

*Arsenious Acid Solution.*—Weigh out 4.95 gms. pure pulverized white arsenic ( $\text{As}_2\text{O}_3$ ), transfer to a litre flask add about 25 gms. pure crystallized sodium carbonate, and 200 c. c. water. Boil gently, with frequent shaking until all is dissolved, cool, and dilute up to the litre

mark. One c. c. of this solution corresponds to 0.00355 available Cl, as may be seen from the following:



The four atoms of available chlorine in the bleaching powder correspond to the two atoms of O taken up by the  $\text{As}_2\text{O}_3$ .

Molecular weight of  $\text{As}_2\text{O}_3 = 198$

Molecular weight of  $\text{Cl}_2 = 142$ .

Since 1 c. c. of the arsenious solution contains

$$0.00495 \text{ gm. As}_2\text{O}_3 = \frac{4.950 \text{ gms. taken}}{1000 \text{ c. c. in 1 litre}}; \text{ then,}$$

$$198 : 142 = 0.00495 : 0.00355.$$

*Analysis.*—Weigh out 10 gms. of the bleaching powder, transfer to a mortar, add 50 or 60 c. c. of water, and rub to a cream. Allow the heavier particles to subside, decant the turbid supernatant fluid, add more water, rub up again, and continue thus until all the powder has been transferred to a litre flask. Fill the flask up to the mark, pour the contents into a beaker, mix it well, and take out 50 c. c. at a time for the analysis. The solution will always remain turbid, but this cannot be avoided, and does not interfere with the accuracy of the results, provided it is uniformly mixed. Into the 50 c. c. taken, run the arsenious solution, from a burette, until a drop of the solution taken out on a rod no longer produces a blue spot on the iodized starch paper, which has been previously moistened and spread out upon a white plate.

The calculation is readily made. Fifty c. c. of bleaching powder solution, made in the way described, is equivalent to 0.5 gm. Suppose this takes 45 c. c. of the arsenious solution. Since 1 c. c. arsenious sol. = 0.00355 gm. available Cl, 45 c. c. =  $(45 \times 0.00355) = 0.15975$  gm. available Cl.

If then 0.5 gm. bleaching powder = 0.15976 gm. Cl,

$$1 \text{ gm.} = 0.3195 \text{ gm.,}$$

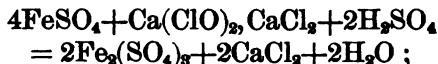
or the bleaching powder contains 31.95 per cent of available chlorine.

## CHLORIMETRY (IRON METHOD).

Weigh out 10 gms. bleaching powder, place in a mortar, add 50 or 60 c. c. water, rub to a cream, allow the coarser particles to settle, pour off the turbid supernatant fluid into a litre flask, add more water, rub again, etc., until all the powder has been transferred to the flask, fill up to the mark, pour the solution into a beaker, and mix well; take out 50 c. c. for the analysis.

Weigh out in the mean time 0.325 gm. piano-forte wire (= 0.324 gm. Fe) and dissolve it in 2 c. c. conc.  $\text{H}_2\text{SO}_4$  diluted with 10 c. c. water in a small valved flask. Cool, fill the flask with cold water, and pour into a large beaker. Now add 50 c. c. of the turbid bleaching powder solution, pouring it in slowly, stirring all the time. Dilute to about 500 c. c. Then, by means of a standardized solution of potassium permanganate (prepared as described under Ammonio Ferric Sulphate, p. 42), determine the amount of iron still remaining in the ferrous form.

The reaction is :



or four atoms Fe correspond to four atoms Cl, 56 parts Fe equivalent to 35.5 parts Cl.

The mode of calculating results is best shown by example.

Suppose 1 c. c. of the permanganate was equivalent to 0.003 gm. Fe, and that it took 23.8 c. c. of that solution to oxidize the ferrous iron not acted upon by the bleaching powder used, in an amount equivalent to 0.5 gm. 23.8 c. c. permanganate correspond to  $(23.8 \times 0.003)$  or 0.0714 gm. Fe remaining unoxidized. Then  $0.324$  (Fe taken) —  $0.0714$  (Fe unoxidized) =  $0.2566$  gm. Fe oxidized by bleaching powder. Since 56 parts Fe correspond to 35.5 parts Cl, we have the proportion :

$$56 : 35.5 = 0.2566 : 0.1601 \text{ gm. available Cl.}$$

0.5 gm. bleaching powder contains 0.1601 available Cl

1 gm. contains 32.02,

or 32.02 per cent available Cl.

## CHAPTER XXXVII.

### ACETATE OF LIME.

The best method of analysis consists in distilling a weighed quantity of the sample repeatedly with excess of hydrochloric acid, and in the distillate determining the acidity, and, since some of the hydrochloric acid distills over, that must also be determined and subtracted from the amount of acid found. (Fres., *Zeitschrift*, V., 315.)

The process is as follows:

Weigh out 10 gms. of the sample, wash it into a small retort with 30 c. c. of water, connect the retort with a good Liebig condenser, add 8 c. c. hydrochloric acid, and distill to small bulk. Then add 30 c. c. of water, and distill again. Repeat this operation at least once more. Combine all the distillates and make the volume up to 500 c. c. By this time, you will have all the acetic acid from the sample as acid in the distillate. Take two portions of 100 c. c. each from the distillate. In one portion (representing 2 gms. of the sample), determine the acidity by titration with normal potassium hydrate solution. The result would show the amount of acetic acid obtainable from 2 gms. of the sample, were it not that some of the hydrochloric acid used has also distilled over. Therefore, in the other 100 c. c. we must determine the amount of hydrochloric acid present. For this we use the tenth normal argentic nitrate solution (volumetric). The solution must, however, be first rendered neutral. For this purpose we use pure calcium carbonate in excess, which must be carefully tested for chlorides, none of which, of course, should be present. About 5 gms. of calcium carbonate will be amply sufficient. Stir it in well, warm up the solution, add a few drops of potassium chromate, and test with the tenth normal silver nitrate solution as described (p. 215).

Since we use a tenth normal solution, divide the number of c. c. used by 10, and then subtract the result from the number of c. c. of normal potassium hydrate solution used. The remainder gives the number of c. c. of potassium hydrate solution neutralized by the acetic acid from 2 gms. of the sample. From this, the amount of acetic acid and percentage of pure acetate of lime present can be readily calculated.

For example, suppose

100 c. c. of distillate neutralized 19.9 c. c. normal KHO,  
and 100 c. c. " " " 5 c. c. tenth n. AgNO<sub>3</sub>.

Then,  $19.9 - 0.5 = 19.4$  c. c. normal KHO neutralized by  
the acetic acid from 2 gms. of the sample,

$19.9 \times 0.06$  (equivalent. of  $\text{HC}_2\text{H}_3\text{O}_2 = 60$ ) = 1.194 gms. of  
acetic acid in 2 gms. of the sample,

$1.194 \times 5 = 5.97$  gms. acetic acid in 10 gms. of sample,  
or  $\times 50 = 59.7$  " " " in 100 " " "

Then  $(2\text{HC}_2\text{H}_3\text{O}_2 : \text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 =) 120 : 158 = 59.7 : x$ .

$x = 78.605$  per cent  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  in the sample.

(For other methods, see Fres., *Zeitschrift*, XIII., 153, and  
*Am. Chem.*, VI., 294.)



## CHAPTER XXXVIII.

### GUANO.

*Phosphoric Acid.*—Fuse 1 gm. with 5 gms. sodium carbonate, and 5 gms. nitrate in a platinum crucible over a Bunsen burner, removing the flame as soon as the fusion is complete, which should be in about half an hour. Remove the contents of the crucible with hot water, acidulate with nitric acid, and boil. The crucible can be cleaned with dilute nitric acid without injury. Filter out any siliceous residue which may remain undissolved, dilute the solution up to 1 litre, and determine phosphoric acid in one fifth (200 c. c.) by means of ammonium molybdate, as usual, using about 50 c. c of the molybdate solution.

*Ammonia.*—To determine the ammonia or nitrogen, select a tube of hard glass, 15 or 18 inches long, draw one end of it to a fine point, and to the other end fit tightly a cork, through which is passed a tube bent at right angles, the other end of which passes through a cork closing tightly one arm of a bulbed U-tube. Into the combustion-tube first slip a loosely-fitting plug of asbestos previously ignited, and then some three or four inches of dry soda lime. Weigh out 1 gm. of the guano, pulverize coarsely some of the soda-lime in a mortar, mix this soda-lime with the guano, and introduce the mixture into the combustion-tube. Enough soda-lime must be taken to make the charge fill the tube to within three or four inches of the open end. Then fill up with soda-lime to within about an inch of the end, place another plug of ignited asbestos at the end, and close with the cork carrying the tube.

Now run into the bulbed U-tube 10 c. c. of half-normal sulphuric acid from a burette, adjust the cork carrying the connection to the combustion-tube, and lay the com-

bustion-tube in the trough of the combustion-furnace, supporting the bulb-tube by a clamp. Begin to heat at the forward end (nearest the cork), and get the soda-lime, which is unmixed with the charge, white hot before the heat is applied to the charge mixed with the guano. Then carry the heat slowly back until the entire contents of the tube are at a white heat. Avoid, however, heating the end which is drawn to a point, lest the pressure in the tube cause it to blow out. Keep up the heat until no more bubbles of gas are forced through the acid in the bulb-tube. Then connect the other limb of the bulb-tube with an aspirator, start the aspirator slowly, and then break off the fine point of the combustion-tube, at the same time removing the heat. Draw a slow current of air through the tube until it is well cooled down, and then disconnect the bulb-tube and pour the contents into a beaker, rinsing it out well. Add a few drops of cochineal solution, and by means of normal KHO solution determine how much of the sulphuric-acid solution used has been neutralized by the ammonia thus obtained from the guano. From the data thus obtained the percentage of ammonia or nitrogen may be readily calculated. Thus, suppose 8 c. c. of the sulphuric acid remained unneutralized, 2 c. c., then, have been neutralized by the ammonia; 1 c. c. =  $0.049 \text{ H}_2\text{SO}_4 = 0.017 \text{ NH}_3$ , or = 0.014 N, and the guano contains  $2 \times 100 \times 0.017 = 3.4$  per cent  $\text{NH}_3$ , or 2.8 nitrogen (*vid.* Fres., § 186, § 187.)

*Sulphuric Acid.*—Fuse 1 gm. with 5 gms. sodium carbonate and 2 gms. nitrate, in a platinum crucible over a Bunsen burner. Wash the fused contents as completely as possible from the crucible with hot water, rinse out the crucible with hydrochloric acid, add it to the solution, acidulate with hydrochloric acid, boil, filter if necessary, and determine sulphuric acid with barium chloride as usual.

*Water.*—Dry 1 to 2 gms. to constant weight, at  $120^\circ \text{C.}$ , in a weighed capsule. The loss is *water*. Then ignite the

capsule at strong red heat to constant weight. The loss is *organic and volatile matter*, including ammonia. Deduct the ammonia found elsewhere, the difference is *non-nitrogenous organic and volatile matter*. Of course, this is only approximate. The residue after igniting is mineral matter, including phosphoric acid. Subtract the phosphoric acid found. The difference is  $\text{CaO}, \text{MgO}, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SO}_3, \text{SiO}_2$ . Report as *mineral matter*.  $\text{SO}_3$  may be driven out by the ignition, if there is no more than enough  $\text{CaO}$  and  $\text{MgO}$  to saturate the phosphoric acid. A qualitative test on a hydrochloric acid solution of the ignited residue will show whether all the  $\text{SO}_3$  has been expelled.

## REPORT.

Phosphoric acid ( $\text{P}_2\text{O}_5$ )*.....	.....
Ammonia ( $\text{NH}_3$ )†.....	.....
Sulphuric acid ( $\text{SO}_3$ ).....	.....
Water ( $\text{H}_2\text{O}$ ).....	.....
Mineral matter.....	.....
Non-nitrogenous organic and volatile matter.....	.....

\* Equivalent to phosphate of lime.....

† “ “ nitrogen.....

## CHAPTER XXXIX.

### RAW SUGAR.

The points usually determined in the ordinary commercial analysis are the amount of crystallizable cane sugar, glucose, water, and ash.

The usual method of determining the amount of crystallizable cane sugar is by the saccharimeter or polariscope, an instrument whose use depends upon the different action of solutions of sugar on polarized light, and so constructed that the per cent of cane sugar is read off directly upon the scale.

A certain amount of sugar to be examined (for the ordinary Soliel saccharimeter, 26.048 gms.), is dissolved in 80 c. c. of cold water, 2 or 3 c. c. of basic acetate of lead added, the solution diluted to exactly 100 c. c., and filtered through a large, dry, corrugated filter. The basic acetate (subacetate or triplumbic acetate), is prepared by digesting, at a moderate heat, 7 parts of finely powdered litharge, 6 parts of neutral lead acetate, and 30 parts of water. If the basic acetate does not clear the solution, or the solution filters badly, add a few drops of solution of sodium sulphate, prepared by dissolving 1 part of the salt in 5 parts of water. If any salt of lead pass through the filter, making the filtrate turbid, dip a rod into acetic acid, and stir the liquid with it. This will dissolve the lead salt and clear the solution.

If the filtered liquid is too much colored for the saccharimeter, filter it through bone coal equivalent in bulk to 8 or 10 c. c. The coal should be previously ground moderately fine, and heated for a few minutes, to a point just below redness, to expel moisture. Care must be taken not to heat the bone-black enough to burn the carbon, and turn it white, as it will then lose the power of decoloriz-

ing sugar solutions. As the coal has the power of absorbing sugar from the solution, thereby rendering it weaker, the filtrate should be poured back on the filter several times before using it in the saccharimeter.

The tube intended to hold the sugar solution should be first washed out with the same, and filled slowly to avoid the presence of bubbles of air. The glass caps should not be pressed on the ends of the tube with the finger, but slid on gently and cautiously, so as to exclude all air.

To adjust the saccharimeter, fill the tube with pure distilled water, and turn the instrument, until the semi-disks are of the same color. It should then read zero. Now fill the tube with the solution to be tested, having previously washed it with the same. The 2 semi-disks will no longer have the same color. Turn the instrument by means of the button, arranged for the purpose, until they have the same color, and read on the scale the per cent of cane sugar.

It is well also to test the instrument with a solution of sugar, of known value. The color to be used depends upon the preference of the operator. The rose tint is best adapted to most eyes, and has the advantage, that, with the slightest change in the instrument, one semi-disk becomes instantly red, and the other green.

The amount of cane sugar in a sample of raw sugar can be estimated by first determining the per cent of invert sugar in a portion by the copper solution, as directed later, and then, after converting a portion entirely into invert sugar, again determining the per cent. The difference in the results is equivalent to the glucose produced by the conversion, which is to be calculated to cane sugar. One hundred parts of invert sugar correspond to 95 parts of cane sugar.

To invert the cane sugar, dissolve 1 gm. of the sugar in 100 c. c. of water, add 1.2 c. c. of concentrated sulphuric acid, and heat on a water-bath for half an hour, replacing,

from time to time, the water lost in evaporation. Neutralize the free acid with a dilute solution of sodium carbonate, dilute to 200 c. c., and proceed as directed.

The determination of glucose requires a solution of copper sulphate, and an alkaline solution of Rochelle salt (sodium and potassium tartrate). These solutions, when mixed, constitute what is called Fehling's solution. It is better, however, to keep them separate (combining only when required), as the mixture is apt to decompose, if kept long.

To prepare the copper solution, dissolve 34.640 gms. of copper sulphate in 200 or 300 c. c. of distilled water, cool, dilute to exactly 500 c. c., and keep in a glass-stoppered bottle. Five c. c. of this solution will then correspond to 0.05 gm. grape sugar. To prepare the Rochelle salt solution, dissolve 63 gms. of pure sodium hydrate in about 400 c. c. of distilled water, add 187 gms. of Rochelle salt, heat on a water-bath, with frequent stirring, until all is dissolved, cool, dilute to exactly 500 c. c. and keep in a glass-stoppered bottle.

To make the analysis, introduce 5 c. c. of the copper sulphate solution, 5 c. c. of the Rochelle-salt solution, and 5 c. c. of water, into a 10-inch test-tube or tall narrow beaker, and also 2 or 3 small fragments of washed and ignited pumice-stone, to prevent bumping of the fluid when heated, boil and add (little at a time), from a burette, the sugar solution to be tested, which should not contain more than 0.5 per cent of sugar. If, upon trial, it is found that all the copper is precipitated by less than 10 c. c. of the sugar solution, dilute the solution with an equal quantity of water and repeat the test. If, on the contrary, it is found that more than 25 c. c. are required, make a solution of the sugar of twice the strength, and repeat. The liquid must be kept alkaline. Toward the end of the operation, a slight cloud is formed upon adding the sugar solution; at the close, the fluid loses its blue color, becoming nearly, if not quite, colorless. If excess of sugar solution is

added, the fluid becomes yellow, and brown if very great excess is added. Violette says that the average of the readings when the cloud forms, and when the fluid becomes yellow, is the true one.

To test the copper-sulphate solution, dry at  $100^{\circ}$  C. some pure powdered cane sugar, weigh 1 gm., dissolve it in 100 c. c. of water, add 1.2 c. c. of pure sulphuric acid, heat on a water-bath for half an hour, cool, neutralize with sodium carbonate, dilute to exactly 200 c. c., and titre with it 5 c. c. of the copper-sulphate solution mixed with 5 c. c. of the Rochelle-salt solution and 5 c. c. of water. If the solution of copper sulphate is accurate, it should require 9.5 c. c. of the sugar solution.

To determine moisture, dry a weighed quantity of the sugar to constant weight, at  $100^{\circ}$  C. It is well not to take more than 0.5 gm. of sugar, as the operation is sometimes very tedious, where a large quantity is used, and the danger of decomposing the sugar by long-continued heating great. The heat must not exceed  $105^{\circ}$  C., as a higher temperature will caramelize the sugar.

In determining the ash, different methods are used. The first consists simply in weighing out 3 or 4 gms. in a platinum dish, and burning at a low red heat until the ash appears white. This operation is extremely tedious, and involves some loss of alkaline salts in consequence of the prolonged exposure to a high temperature necessary. A method much used in France consists in adding a few c. c. of concentrated sulphuric acid to 3 or 4 gms. of the sugar in a platinum capsule, and incinerating as before. From the weight of the ash thus obtained one ninth is subtracted, and the figure remaining is reported as the ash of the sugar. The most accurate method consists in carbonizing the sugar at a high heat for a short time, pulverizing the carbon thus obtained, extracting from it the alkaline salts by boiling with water, filtering, evaporating, and gently igniting the filtrate in a platinum dish, and then incinerating the carbonaceous matter insoluble in water.

This gives the proportion of soluble and insoluble ash, their sum being, of course, equal to total ash. The three methods give results sometimes differing widely from one another when tried on the same sample. In any case, where carbonization of the sugar begins, the sugar is apt to boil up, and care must be exercised lest some loss may be experienced in consequence.

To examine sugar or molasses for artificial glucose (made from starch) weigh out 18.86 gms. of the sample to be tested, dissolve in water, invert by acidulating and heating, cool, neutralize with sodium carbonate, dilute to 100 c. c., and examine in the polariscope at a temperature of 92° C. The percentage of artificial glucose present will then be indicated on the scale. (See *Journ. Am. Chem. Soc.*, Vol. I., p. 2.)



## CHAPTER XL.

### SUGAR (ULTIMATE ANALYSIS).



*Percentages of C, H, and O.*—The carbon and hydrogen are determined at one operation by combustion in a stream of dry oxygen, the resulting  $CO_2$  and  $H_2O$  being caught in suitable apparatus and weighed in those combinations. The oxygen is determined by difference. Select a tube of hard glass about 28 inches long, and 5 or 6 tenths of an inch internal diameter, fit to each end corks through which are passed tubes of about 1 tenth inch internal diameter, and 3 or 4 inches in length. About 2 inches from the front end of the tube (the end to be attached to the apparatus for absorbing  $CO_2$  and  $H_2O$ ), place a plug of asbestos, previously ignited to remove all moisture and carbonaceous material. Back of this plug put enough freshly-ignited  $CuO$  to fill the tube a little more than half, and push down upon this another plug of ignited asbestos. Provide at the rear end of the tube two bottles, with corks and tubes, for drying the  $O$  and removing from it any traces of  $CO_2$ , it may contain, by bubbling it through the bottles, containing, respectively, concentrated  $H_2SO_4$  and strong  $KHO$ , having the sulphuric acid next to the tube. For the front end, have a tube filled with neutral calcium chloride in fragments, through which a current of dry carbon dioxide has been passed for some time, followed by a current of dry air. To absorb the carbon dioxide, prepare a U-tube, filled with soda-lime, constructed in the same manner as given for the determination of  $CO_2$  in limestone (p. 63) or carbon in iron (p. 106). The sugar, being previously dried thoroughly at  $100^\circ C.$ , 0.250 gm. is then to be weighed out in a platinum boat. Weigh the calcium-chloride tube and the soda-lime tube. Connect the combustion-tube (laid in the trough of the combustion-fur-

nace) at the rear end with the bottles of sulphuric acid and potassium hydrate, and at the front end directly with the aspirator, heat it to redness, and then draw a current of air through it until cool. Then introduce the platinum boat into the rear end, replace the cork, and connect the calcium-chloride tube and soda-lime tube at the front end, connecting the last with the aspirator. Draw a slow current of air through the tube, and begin to heat the front end of the  $\text{CuO}$ , carrying the heat slowly backward toward the boat containing the sugar. At the same time, keep the rear end over the tube moderately, carrying the heat slowly forward. Arrange it so that the  $\text{CuO}$  shall be heated highly before the sugar begins to burn. Just before the heat reaches the boat, attach the tube from the oxygen cylinder, and force a slow current of the gas through the tube. Heat the sugar very moderately, so that it will burn slowly and not force the gases off too rapidly. When it is completely consumed, which may be seen by the disappearance of the black carbon, remove the heat, disconnect the oxygen cylinder, and draw a current of air through it until it is cool. Then detach the tubes and weigh. The increase in weight of the calcium-chloride tube represents water, from which the percentage of hydrogen may be calculated, the increase in weight of the soda-lime tube represents the carbon dioxide, to be calculated to C.

## CHAPTER XLI.

### TURPENTINE (ULTIMATE ANALYSIS.)



*Percentages of C and H.*—The process pursued is essentially the same as that in the ultimate analysis of sugar. A few modifications only are necessary, since in this case we are dealing with a volatile liquid instead of a solid. The pieces of apparatus necessary, are the same as for the sugar analysis, with the exception of the platinum boat in which the sugar is weighed. Instead of this a small bulb of thin glass is prepared, the "tail" of which is drawn to a long fine point. The extreme point is then broken off, so as to leave an opening into the interior, which should be as fine as a hair. The bulb is weighed and then warmed, and the end being immersed below the surface of some turpentine, the contraction of the air in the bulb, as it cools, will draw some of the liquid into the bulb. Before it is quite cold, withdraw the point from the turpentine, that the contraction may draw the liquid out of the "tail," leaving it clear. Then wipe the "tail" dry, and seal the end by a moment's exposure to a blow-pipe flame. The glass should be so thin that this can be readily accomplished. Weigh again. The increase in weight of the bulb gives the weight of the turpentine taken. Half-fill the combustion-tube with ignited copper oxide as before, drop in the bulb containing the turpentine, just crack it by a light blow from a glass rod, introduced for the purpose, and immediately pour down upon it some more copper oxide which has been ignited and cooled out of contact with the air. Conduct the remainder of the operation as in the case of sugar, carrying the heat back more slowly and carefully. A longer tube than that used for sugar analysis may be used with advantage. Carry the heat quite to the end of the copper oxide before stopping the operation.

## CHAPTER XLII.

### BONE-BLACK.

*Water*.—Dry 1 gm. at  $170^{\circ}$  C. to constant weight. The loss is water.

*Carbon Dioxide*.—Introduce into the flask of a  $\text{CO}_2$  apparatus 5 gms. of the finely pulverized black, add 30 c. c. dilute hydrochloric acid, and determine the carbon dioxide by absorption in soda-lime. Calculate to  $\text{CaCO}_3$ .\*

After the determination of the carbon dioxide in the manner first given (by absorption with soda-lime) pour the contents of the flask upon a filter and wash thoroughly. There will then be a *residue* and a *solution*.

The residue consists of sand, clay, carbon, and insoluble organic matter. Wash it from the filter into a weighed platinum dish, allow it to settle, decant off the clear fluid as closely as possible without disturbing the residue, evaporate, dry at  $170^{\circ}$  C., and weigh. Weight = *sand, clay, and carbon*, plus dish. Ignite until all carbon is burned off, and weigh again. Weight = *sand and clay*, plus dish. Difference from above weight reported as *carbon*. In the *solution* add barium chloride, to precipitate the sulphuric acid, filter off, weigh the  $\text{BaSO}_4$ , and calculate the sulphuric acid to  $\text{CaSO}_4$ . Dilute the filtrate to 500 c. c., and divide into two parts;  $A = 100$  c. c.,  $B = 400$  c. c.

*A*.—Dilute to 500 c. c., and take 100 c. c. (representing one

---

\* In most, if not all, sugar-houses, the common method of determining carbon dioxide is a volumetric process, the volume of gas evolved being measured by an instrument invented by Dr. C. A. Scheibler, a full description of which will be found in Fres., *Quant. Anal.*, § 287, or in Crookes's *Special Methods*, p. 890. From the latter work, p. 897, the following table of corrections for temperature of the volume of gas obtained has been taken :

TABLE FOR THE PERCENTAGE ESTIMATION OF THE CARBONATE OF CALCIUM CONTAINED IN ANIMAL CHARCOAL, CALCULATED FROM THE VOLUME OF THE CARBONIC ACID.

Observed Volume of Carbonic Acid.	DEGREES OF TEMPERATURE (CENTIGRADE).																		
	12°.	13°.	14°.	15°.	16°.	17°.	18°.	19°.	20°.	21°.	22°.	23°.	24°.	25°.	26°.	27°.	28°.	29°.	30°.
1.....	0.80	0.80	0.79	0.79	0.79	0.79	0.78	0.77	0.77	0.77	0.76	0.76	0.76	0.75	0.75	0.74	0.74	0.73	0.73
2.....	1.88	1.87	1.86	1.86	1.85	1.85	1.84	1.83	1.82	1.81	1.80	1.79	1.78	1.77	1.76	1.75	1.74	1.73	1.72
3.....	2.95	2.94	2.92	2.91	2.90	2.89	2.87	2.86	2.85	2.83	2.82	2.80	2.79	2.77	2.76	2.74	2.73	2.72	2.71
4.....	4.01	4.00	3.98	3.96	3.94	3.93	3.91	3.89	3.87	3.85	3.83	3.81	3.79	3.77	3.75	3.73	3.71	3.70	3.68
5.....	5.07	5.05	5.03	5.00	4.98	4.96	4.93	4.91	4.89	4.86	4.84	4.81	4.79	4.76	4.74	4.71	4.69	4.67	4.65
6.....	6.11	6.09	6.06	6.03	6.01	5.98	5.95	5.92	5.89	5.86	5.83	5.81	5.78	5.75	5.71	5.68	5.65	5.63	5.61
7.....	7.14	7.12	7.09	7.06	7.02	6.99	6.96	6.92	6.89	6.86	6.82	6.79	6.75	6.72	6.68	6.65	6.61	6.58	6.56
8.....	8.17	8.14	8.11	8.07	8.03	8.00	7.96	7.92	7.88	7.84	7.80	7.76	7.72	7.68	7.64	7.60	7.56	7.53	7.49
9.....	9.19	9.16	9.12	9.07	9.03	8.99	8.95	8.90	8.86	8.82	8.77	8.73	8.68	8.64	8.59	8.55	8.50	8.46	8.42
10.....	10.20	10.16	10.12	10.07	10.02	9.98	9.93	9.88	9.83	9.79	9.73	9.68	9.63	9.58	9.53	9.48	9.43	9.39	9.34
11.....	11.20	11.15	11.10	11.05	11.00	10.95	10.89	10.84	10.79	10.74	10.68	10.63	10.57	10.52	10.46	10.41	10.35	10.30	10.25
12.....	12.20	12.15	12.08	12.03	11.98	11.92	11.87	11.81	11.75	11.69	11.64	11.58	11.52	11.46	11.40	11.33	11.27	11.22	11.16
13.....	13.20	13.14	13.08	13.02	12.96	12.90	12.84	12.78	12.72	12.65	12.59	12.53	12.46	12.40	12.33	12.26	12.20	12.14	12.07
14.....	14.20	14.14	14.07	14.01	13.94	13.88	13.81	13.75	13.68	13.61	13.54	13.48	13.41	13.34	13.26	13.19	13.12	13.05	12.99
15.....	15.20	15.13	15.06	14.99	14.92	14.85	14.78	14.71	14.64	14.57	14.50	14.43	14.35	14.27	14.20	14.12	14.04	13.97	13.90
16.....	16.20	16.13	16.05	15.98	15.91	15.83	15.76	15.68	15.61	15.53	15.45	15.37	15.29	15.21	15.13	15.05	14.97	14.89	14.81
17.....	17.20	17.12	17.04	16.97	16.89	16.81	16.73	16.65	16.57	16.49	16.41	16.32	16.24	16.15	16.07	15.98	15.89	15.81	15.73
18.....	18.20	18.12	18.03	17.95	17.87	17.79	17.71	17.62	17.53	17.45	17.36	17.27	17.18	17.09	17.00	16.91	16.82	16.73	16.63
19.....	19.20	19.11	19.03	18.94	18.85	18.76	18.67	18.59	18.50	18.40	18.31	18.22	18.13	18.03	17.94	17.84	17.74	17.64	17.55
20.....	20.20	20.11	20.02	19.93	19.83	19.74	19.65	19.55	19.46	19.36	19.27	19.17	19.07	18.97	18.87	18.77	18.66	18.56	18.46
21.....	21.20	21.10	21.01	20.91	20.81	20.72	20.62	20.52	20.42	20.32	20.22	20.12	20.01	19.91	19.80	19.70	19.59	19.48	19.37
22.....	22.20	22.10	22.00	21.90	21.80	21.70	21.59	21.49	21.39	21.28	21.17	21.07	20.96	20.85	20.74	20.63	20.51	20.40	20.28
23.....	23.20	23.09	22.99	22.88	22.78	22.67	22.56	22.46	22.35	22.24	22.13	22.02	21.90	21.79	21.67	21.55	21.44	21.31	21.20
24.....	24.20	24.09	23.98	23.87	23.76	23.65	23.54	23.43	23.31	23.20	23.08	22.97	22.85	22.73	22.61	22.48	22.36	22.23	22.11
25.....	25.20	25.08	24.97	24.86	24.74	24.63	24.51	24.39	24.28	24.16	24.04	23.91	23.79	23.67	23.54	23.41	23.28	23.15	23.03

fifth of a gm.), add about 10 c. c. conc. nitric acid, evaporate nearly to dryness to expel hydrochloric acid, add 50 c. c. ammonium molybdate, and determine phosphoric acid as usual. Calculate to  $\text{Ca}_3(\text{PO}_4)_2$ .

*B.*—Add 4 or 5 c. c. conc. sulphuric acid, evaporate nearly to dryness, add 25 or 30 c. c. water, and 100 c. c. alcohol. The precipitate is  $\text{BaSO}_4 + \text{CaSO}_4$ . Filter out, wash well with water, from the filtrate boil out the alcohol, reduce the iron with zinc and platinum, as in iron ore, and titre with potassium permanganate. Calculate to  $\text{FeO}$ .

*Nitrogen, chlorine, and alkalies* may sometimes be required.

For *chlorine*, boil 5 gms. with nitric acid, filter, and determine by  $\text{AgNO}_3$  in the filtrate. For *nitrogen* and *alkalies*, see Guano and Superphosphate, pp. 197 and 222.

A mechanical test of the size of the black is frequently made. For this purpose 100 gms. is weighed out and shaken in a series of ten wire sieves, the meshes of which are of gradually decreasing size, thus :

No.	1	has	6	holes to	linear inch.
"	2	"	8	"	"
"	3	"	10	"	"
"	4	"	20	"	"
"	5	"	30	"	"
"	6	"	40	"	"
"	7	"	50	"	"
"	8	"	60	"	"
"	9	"	80	"	"
"	10	"	100	"	"
Fine	"		120	"	"

To get the average fineness of the black, multiply the weight left on each sieve by the number of meshes of that sieve to the inch, add the products together, and divide by 100.

To determine the *weight of a cubic foot* of the black, select a small porcelain capsule, weigh, then fill with the

black, level with the brim without shaking down, weigh again, and then weigh the capsule full of water; and this gives all the data necessary for calculating the specific gravity of the black when lying loosely. From this the weight of a cubic foot may be calculated. That of a cubic foot of water is usually taken as 62½ lbs. (62½ lbs., *Watts's Dict.*, V., 1010.)

To determine the absorptive power of the black—the *porosity*—weigh out 20 gms. in a funnel, drench with water, allow the surplus water to drain off, and weigh again. The amount of water retained shows the degree of porosity.

*Decolorizing Power.*—Make a solution of raw sugar of 10° Bé. (about 1.07 sp. gr.), take 20 to 50 gms. of the sample, and the same amount of a bone-black the power of which is known. Wet the samples down well with the raw-sugar solution, and pass equal amounts of the solution through each sample. Compare the depth of color left in the sugar solutions, after filtration, with one another by means of a Duboscq colorimeter.

*Completeness of burning* is determined by boiling a portion of the sample with solution of sodium or potassium hydrate. The deeper the coloration of the alkaline solution the less complete the burning has been, since organic matters occurring in the coal, which have been incompletely carbonized, impart a strong color to solutions of caustic alkalies.

*Completeness of Washing.*—Wash with hot water, and, after cooling, test the density of the wash-water.

## CHAPTER XLIII.

### COAL.

*Moisture.*—Dry 2 gms. of the coal, finely pulverized, in a weighed platinum crucible at  $115^{\circ}$  C., for half an hour, cool, and weigh. Dry again for 15 minutes at the same temperature, cool, and weigh again. Repeat this until the weight begins to increase, indicating incipient oxidation. From the lowest weight thus obtained calculate the percentage of moisture.

*Volatile Combustible Matter.*—Ignite the above crucible and contents for three minutes (keeping the crucible closely covered) in the strongest heat of a good Bunsen burner, then at once ignite for the same length of time over the blast-lamp, cool, and weigh. The crucible should be kept covered throughout this operation. The loss is volatile combustible with half the sulphur. For anthracite or coals containing no bituminous matter, this operation may be omitted as unnecessary.

*Fixed Carbon.*—Remove the cover, and burn off the remaining carbon over a Bunsen burner until nothing remains but the ash. The loss is fixed carbon with the remainder of the sulphur. The final weight, less the weight of the crucible, gives the *ash*.

*Sulphur.*—Pulverize the coal finely, weigh out 2 gms. and mix it thoroughly in a convex cover with 16 gms. sodium carbonate and 16 gms. sodium nitrate, also finely pulverized. Now, with a spatula introduce a little of the mixture into a large platinum crucible, cover it, and heat until deflagration commences, when the flame should be removed. As soon as the violence of the deflagration has ceased, add a little more of the mixture, and apply the flame again until deflagration again occurs. Repeat this until all of the mixture has been transferred to the crucible. Heat after the last violent deflagration has ceased,



until the mass is in complete fusion to insure oxidation of the sulphur. Dissolve out the contents of the crucible in boiling water, acidulate with HCl, boil to remove the lower oxides of nitrogen, if anything remains undissolved, filter and wash. In the solution, precipitate the sulphur (now present as sulphate) with  $\text{BaCl}_2$  in the manner already given (p. 18.)

The most convenient method of keeping the notes on a coal analysis are as follows, an example being given to show how the calculation is made :

Weight of crucible and coal.....	32.0000	gms.
“ “ crucible.....	30.0000	“
Coal taken .....	2.0000	“
Weight of crucible + coal.....	32.0000	
“ “ “ after drying.....	31.9920	
Loss = $\text{H}_2\text{O}$ .....	0.0080	0.40 per cent.
Weight of crucible + coal dried.....	31.9920	
“ “ “ ignited (closed).....	31.4480	
Loss = volatile combustible + $\frac{1}{2}$ S....	0.5440	27.20 “
Weight of crucible + coal ignited (closed)....	31.4480	
“ “ “ ignited (open) .....	30.1000	
Loss = fixed carbon + $\frac{1}{2}$ S.....	1.3480	67.40 “
Weight of crucible + contents ignited (open).	30.1000	
“ “ .....	30.0000	
Residue = ash.....	0.1000	5.00 “
Sulphur.....	1.00	“

## REPORT.

Moisture.....	0.40 per cent.
Volatile combustible (27.20 less 0.5 or $\frac{1}{2}$ S).....	26.70 “
Fixed carbon (67.40 less 0.5 or $\frac{1}{2}$ S).....	66.90 “
Ash.....	5.00 “
Sulphur.....	1.00 “
	100.00

*Weight of a Given Volume of the Coal* (1 cubic yard).—By weighing a fragment of the coal suspended from the balance by a hair in air and then in water the specific gravity may be obtained. The weight of a cubic yard may

then be calculated, *e. g.*: Suppose the specific gravity to be 1.3488.

Now, 1 cubic foot of water weighs 62.355 lbs. (*Watts's Dict.*, V., p. 1010), and 1 cubic yard weighs  $62.355 \times 27 = 1683.585$  lbs.  $\therefore$  1 cubic yard coal weighs  $1683.585 \times 1.3488 = 2270.819$  lbs. or, leaving off the decimals 2271 lbs. The weight of 1 cubic foot of water may be regarded as  $62\frac{1}{4}$  lbs.

*Ultimate or Elementary Analysis of Coal.*—This is conducted in the same manner as for sugar, which see p. 230.

*Heating Power.*—Berthier's method, by the reduction of lead oxide (*Handb. der Met. Analyt. Chem.*, I., 207; Kerl., *Hütten-kunde*, I., 218), is thus described:

Mix 1 gm. of the finely pulverized coal carefully with not less than 20 or more than 40 times its weight of finely sifted litharge containing no metallic particles, place the mixture in a small crucible, and cover it with 30 times its weight of litharge. That the mixture may not boil over, the crucible should be only about half full. Cover the crucible, and heat gradually in a muffle or wind furnace to red heat. If the heat is raised too rapidly, combustible gases escape, or the mass may boil over. In using a wind furnace, the crucible should be placed on a fire-brick, resting on the grate bars supporting the glowing coals. Shake coals around it until only the top of the crucible projects. When the mass, which at first swells up, is fused, cover the crucible entirely with coals, and increase the heat for ten minutes to collect the lead in a button, and then take it out. The whole operation lasts from forty-five minutes to one hour. Break up the crucible, clean the button from adhering lead oxide by means of a brush, and weigh. To obtain a reliable average make two to four tests. Forchammer (*Bgwfd.*, XI., 30) recommends, instead of litharge, a mixture of 3 parts litharge with 1 part lead chloride, which fuses more readily and requires only ten minutes for the operation. As unity we

refer to carbon, which reduces 34 times its weight of lead. Sugar carbon gives nearly this quantity of charcoal; with 1 to 1.5 per cent ash, only 29 to 30 parts. If we assume 1 caloric as 8086 (Favre and Silbermann) every part of lead produced =  $\frac{8086}{34} = 230$  heat units. Since this is based upon Welters's\* law, it gives no absolutely correct results, but they do not differ appreciably from the truth, so that this process on account of its simplicity is still of value, and it is still frequently used. (Winkler *Erdm. Jr. für Prakt. Chem.*, XVII., 65; V. Hauer, *Oesterr. Zeitschr.*, CLIII., 34, 156, 249.) The results are at most one ninth too low, as estimated against the calculation from elementary analysis, and according to Stölzel (*Dingl. Polyt. J.*, CXLVI., 138) are the closer the higher the percentage of carbon, and the greater the care exercised to avoid loss of carbon monoxide.

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\* Welters's law may be briefly stated thus: The absolute heating effects of carbon and hydrogen stand in direct relation to the amounts of oxygen taken up in burning. Thus, one part by weight of H stoichiometrically calculated requires thrice as much O as one part of C, *e. g.*:

2 parts hydrogen take 16 parts O to form  $H_2O$  or 1 pt. H takes 8 pts. O.

12 " carbon " 32 " " "  $CO_2$  " 1 pt. C "  $2\frac{1}{2}$  " O.

∴ Heating effect of H : Heating effect of C = 3 : 1.

Experimental researches show the absolute heating effect of H as compared with C to be 4.2 : 1 (Favre and Silbermann *ib.*).

## CHAPTER XLIV.

### PETROLEUM.

Petroleum consists of a mixture of hydrocarbons, principally of the so-called paraffine series,  $C_nH_{2n+2}$ , in which the temperatures of boiling or melting increase as the number of atoms of carbon in the molecule increase. Thus, the first four of the series are gaseous at ordinary temperatures, the next two or three boil at a temperature below that of boiling water, the rest at a still higher temperature. As the number of carbon atoms in the molecule increase, the boiling point becomes higher and higher. Those members of the series containing twenty atoms of carbon or more in the molecule are solid at ordinary temperatures (commercial paraffines), etc. (*vid.* Fowne's *Elementary Chem.*).

The chief value of a petroleum lies in the amount and quality of burning, and heavy paraffine oil which can be obtained from it. This is determined by subjecting the oil to what is called "fractional distillation," keeping the portions distilling off at different temperatures apart from each other, and then determining the amount and quality of the fractions. What distills off first is known as the naphtha, and is inferior in value. The last portions, after distilling off the heavy paraffine oils, have also little or no value. The process is thus conducted:

The gravity of the oil at 60° F. is first taken. Then 500 or 1000 c. c. of the oil, preferably the larger quantity, is weighed, and placed in a retort connected with a good Liebig condenser. A cork, carrying a thermometer which will register temperatures at least as high as 500° F., is then fitted to the tubulure of the retort and heat is applied. The oil is gradually raised to the temperature of boiling. Being a mixture of hydrocarbons having different boiling points, the temperature does not remain constant, but

steadily increases. As soon as the thermometer indicates 150° F., the receiver is changed, and another is substituted. This is again changed at 250° F. These first two fractions are the light and heavy naphtha. The fraction between 250° and 400° is the light-, and that between 400° and 500° the heavy-burning oil. If it is only desired to determine the quantity and quality of the illuminating oils which the petroleum will yield, we may stop here. If it is desirable to go on, the heat is removed for a moment while the thermometer is taken out and replaced by a close-fitting ground-glass stopper. The heat is then replaced, and the distillation continued until but a small amount is left in the retort. In some cases, two or three fractions are made of the last portion coming off after 500°. Having the fractions, the next step is to determine their amount and quality. Measure and weigh each one, and take the specific gravity as a check on the results. It must be remembered that loss is involved in every transfer of the oil from one vessel to another; therefore the best plan is to weigh the receivers for the fractions beforehand. The specific gravity is usually reported in degrees Baumé. Since, however, there are several tables giving the comparison of Baumé degrees and specific gravities which differ from one another more or less widely, it is well also to record the specific gravity, which may be ascertained most readily and accurately by weighing a small piece of glass or brass suspended from a hair in the oil, then in air, and in water.

## REPORT.

Gravity of the oil....°Baumé (= sp. gr....)

The oil was found to contain :

		Temperature.		Per Cent		Gravity	
		Fahr.	By Vol.	By Wt.	Bé.	= Sp. Gr.	
Light.	} Naphtha.....	70° to 150°	.....	.....	.....	.....	
Heavy.		150° to 250°	.....	.....	.....	.....	
Light.	} Burning oil.....	250° to 400°	.....	.....	.....	.....	
Heavy.		400° to 500°	.....	.....	.....	.....	
Paraffine oils.....		500° upward.	.....	.....	.....	.....	
Residue (cokings).....			.....	.....	.....	.....	

Refined burning oils sometimes require to be tested for "flashing" and "burning" points; or, in other words, it may become necessary to determine at what temperature the oil will evolve an inflammable vapor, and at what temperature it will take fire when brought near a flame. The test is made by placing a small portion of the oil in a glass vessel surrounded by water, immersing a thermometer in the oil, and slowly heating the water, which, in turn, imparts heat to the oil. The oil should be frequently stirred to insure uniform heating, and from time to time a small flame is brought near the surface of the oil. The temperature should not be raised faster than  $3^{\circ}$  in five minutes. When the "flashing point" is reached, on the approach of a flame, a light blue flame runs over the surface of the oil, accompanied with a slight explosive sound. The indication of the thermometer is then noted. The heat is still raised until the application of the flame will set the oil on fire, and it will remain burning when the flame is removed. The indication of the thermometer is then noted as the "burning point." The operation should be conducted in a place not exposed to draughts. The flame should not be frequently applied to the surface of the oil, lest the upper layer of the oil should be heated up to the flashing point, while the lower layers, the temperature of which is shown by the thermometer, are still below that temperature. A good quality of burning oil should not flash below  $110^{\circ}$  F.

## CHAPTER XLV.

### EXAMINATION OF ILLUMINATING GAS.

The tests most frequently made or required in determining the value of illuminating gas are : Specific gravity, illuminating power, sulphur and ammonia.

*The Specific Gravity* may be determined by Bunsen's method of weighing a glass globe when exhausted by an air-pump, when filled with air, and when filled with the gas, and from the data obtained calculating the result. The more convenient and more common method at present in gas-testing stations is the Schilling effusion test, in which the times of effusion of equal volumes of gas and air through a fine hole in a thin, metallic plate are compared. The principle upon which it depends being that the specific gravities of two gasses passing through such an opening are proportionate to the squares of the times of effusion. . As the specific gravity of air is taken as 1.000, if a given volume of air escapes in 139 seconds, and the same volume of gas requires but 90 seconds, the calculation would be :

$$\begin{aligned}\text{Sp. gr. of air (= 1) : Sp. gr. of gas} &= (139^2 =) 19,321 \\ &: (90^2 =) 8,100\end{aligned}$$

$$\text{Sp. gr. of gas} = \frac{8,100}{19,321} = 0.419$$

*Illuminating Power.*—The methods most relied upon in taking the illuminating power depend upon the principle that the intensity of light varies inversely as the square of the distance from its source. If, then, between two lights which are to be compared we place a light screen and move it back and forth until both sides are equally illuminated, its respective distances from the two lights will be as 1 to 1 if they are equal in intensity ; as 1 to 4 if one is twice as bright as the other ; as 1 to 9 if one is thrice as bright, and so on.

If one of these lights is assumed as a standard, we have then a measure of the illuminating power of the other in terms of the standard.

*The Standard* adopted is the light derived from a sperm candle, of which six weigh one pound, and each of which will burn 120 grains per hour. These candles are manufactured at present expressly for this purpose. When cast in the moulds they are made slightly tapering from the butt in order to facilitate their removal when cooled. This taper should be removed by drawing them through a plate like a wire-drawing plate, that they may be uniform in calibre. This process is sometimes neglected by the manufacturer, so that each candle should be examined before using to see that it is of uniform diameter throughout. If the candle—as is frequently the case—does not burn exactly 120 grains per hour, a correction may be made for the variation, provided it does not exceed 6 grains on either side of this rate, *i. e.*, is between 114 and 126 grains. If those limits are exceeded the results should be rejected.

*The Burner* for the gas was originally required by British acts of Parliament to be “an argand burner having 15 holes and a 7-inch chimney.” This description was, however, not found to be sufficiently close, as a large variety of burners might answer this description, and give very different results with the same gas.

A pattern, however, answering this description was manufactured, and for a long time both here and in England known as the “Standard London argand.” More recently, however, the question of standards for gas has been overhauled in England, and standard burners manufactured by Sugg, of London, have been adopted, of which the material dimensions of the various parts, &c., are accurately specified. It is sufficient here to state that for gas of under 20 candle power the burner known as “Sugg’s London argand No. 1” is used. This is provided with a steatite (commonly called lava) chamber with 24 holes,



and a chimney of 6 inches in height, and an internal diameter of  $1\frac{1}{4}$  inches. For gas of under 16 candle-power a chimney of  $1\frac{1}{8}$  inches internal diameter, and of the same height, is used with the same burner. For cannel gas and other rich gases, a steatite batswing burner is used. In this country for gas running up to 30 candle power another burner manufactured by Sugg, and similar to his "London argand No. 1," is used, which is provided with 32 holes and a 9-inch chimney.

*Meters.*—The rate at which the gas is to be burned is 5 ft. per hour. As the duration of a test is ordinarily not over 15 minutes, an experimental meter registering to thousandths of a foot is necessary. A wet meter is used in which the water is brought to a given level indicated by a mark on the gauge. In some photometric rooms a clock striking every minute with a preliminary alarm 5 seconds before it strikes is used; but the most recently constructed meters for this purpose are provided with a hand run by clock work, which will travel around the face of the meter with the meter hand, if the gas burns at exactly the rate of 5 ft. per hour, while if it does not, the amount by which the one hand is in advance of the other furnishes a basis for a simple calculation of the rate per hour for which a correction must be made, in calculating the candle power.

*Photometer Bar and Disc.*—The photometer bar is simply the bar on which the disc is moved back and forth between the two lights, and is graduated so that by the aid of a pointer immediately below the disc the candle power observed may be at once read off. The lights are usually placed at 100 inches apart. The disc formerly used was of paper stretched in a small circular frame, oiled except a small spot in the centre. The form at present used is a paper with a star-shaped hole in the centre between two thin plain papers, the whole set in a frame, and inclosed in a box blackened inside to exclude reflec-

tions, and prevent the glare of the lights which are compared from distracting the attention.

*Pressure, etc.*—The pressure at the meter should be equal to half an inch of water, and at the burner should be as nearly zero as possible. Attention is not always given to the barometric pressure, and the temperature of the room in which the tests are made. The barometer should stand at 30 inches, and the temperature should be 60° F. If any great variation from these figures occurs, corrections should be made to obtain the true measurement of the gas passed through the meter.

*The Photometer Room* should have the walls, ceiling and floors, colored dead black to avoid reflections, which would interfere with the correctness of the observations.

In making the test the candle should be first lighted and allowed to burn for five or ten minutes; the gas also should be allowed to burn for about the same length of time, and the rate of burning adjusted with a tangent screw-cock. The candle (or candles, since two are now often used) are counterbalanced by the use of shot or sand, and at the same instant the time is noted. With the most improved forms of apparatus, the candles are balanced and weighed in position. With some other forms, the balance is separate from the rest of the apparatus, and provided with a socket at one end of the beam to receive the candle. The disc is then moved back and forth on the bar until both sides appear to be equally illuminated, and the reading is taken once and sometimes twice a minute. The meter is also observed every minute to insure uniformity of burning of the gas. These readings are of course recorded as fast as made, and after ten or fifteen minutes an average is taken; the amount of candle burned is ascertained by adding grain weights to the pan under the candle socket to replace the weight burned, and the time noted. In this way the candle and gas rates are obtained; the photometer readings are averaged, and where two candles have been used, the figure obtained is doubled. This

gives observed candle power, which must be corrected for both gas and candle rates.

*Correction for Gas and Candle.*—If the gas has burned at the rate of over 5 feet per hour, the observed candle power is too high ; if the gas rate is less than 5 feet it is too low. We therefore correct by a proportion :

Gas rate : 5 ft. = obs. c. p. : c. p. corrected for gas.

This result must again be corrected for candle rate by a similar proportion. If the candle rate is over 120 grains, the reading has been too low ; if under 120 grains, it is too high. The proportion therefore is : 120 : candle rate = c. p. : corrected candle power. These corrections may be made in either order, when, if the arithmetic is correct, the result will be essentially the same. *E. g.*: Suppose the observed candle power to be 17.12, the gas rate 4.9, the candle rate 124 grains :

In correcting first for gas rate,

$4.9 : 5 = 17.12 : \text{candle power corrected} = 17.46.$

Correcting this for candle rate,

$120 : 124 = 17.46 : \text{correct candle power} = 18.04.$

Or, to correct first for candle rate,

$120 : 124 = 17.12 : \text{candle power corrected} = 17.69.$

Then, for gas rate,

$4.9 : 5 = 17.69 : \text{correct candle power} = 18.05.$

Essentially the same result.

*Sulphur.*—This is determined in gas by burning the gas slowly in such a way that the products of combustion mingle with fumes of ammonia or its carbonate, collecting the ammonia compounds of the sulphur thus obtained (sulphate and sulphite), oxidizing them to sulphate, and determining as usual by precipitation with barium chloride. An experiment meter registering to thousandths of a foot is used, and from four to ten feet of gas are burned for a determination, at the rate of from half a foot to one foot per hour. Two forms of apparatus are used, "Letheby's" and "the Referee's." In the first (which is the older form) the gas is burned in a Leslie burner,

which consists of a number of small metal tubes, arranged in a ring like an argand burner. Below the burner is placed a beaker containing ammonia, over which a funnel is inverted, the stem of the funnel coming up through the centre of the burner. Over the burner is a trumpet tube, in shape like a long truncated cone, the upper end of which is turned at right angles and passes through a cork in a horizontal, cylindrical "receiver," shaped like a double-ended bottle, with a shoulder at each end. In the receiver is also placed about 20 c. c. of strong ammonia. To the other end of the receiver is fitted a long tube, about the size of combustion tubing. This tube is not set quite horizontal, but inclined slightly upward so that any liquids condensing in it will flow back to the receiver. It is often also surrounded by a Liebig condenser, to insure more complete condensation.

In the Referee's apparatus the gas is burned in a single hole steatite jet, around which are placed lumps of ammonium sesquicarbonate, while over it is placed a trumpet tube, as in the Letheby apparatus. Instead of the "receiver," however, a tall, glass bubbling-jar is used, filled with marbles, over which a stream of ammonia is made to trickle slowly. The ammonia flows through a tube at the bottom into a beaker placed to receive it. To insure sufficient draught through the marbles it is sometimes well to attach an aspirator to the upper end of the bubbling-jar, and keep up an exhaustion of about one quarter to one half an inch of water.

With either apparatus, after a sufficient amount of gas has been burned; the entire apparatus, trumpet tube and all, are thoroughly washed out; the washings and contents of the receiver, etc., added together; the whole evaporated nearly or quite to dryness, a few c. c. of bromine water added and again evaporated, and finally water added to bring the solution up to a convenient bulk, and the sulphate precipitated as usual with barium chloride.

The sulphur calculated from the weight of barium sul-

phate thus obtained is reckoned to so and so many grains per hundred feet of gas, and is so reported. The amount depends on the character of the materials used in making the gas, and the kind and efficiency of the methods of purification used. The amount depending upon these conditions may be from five to over forty grains per 100 feet.

*Ammonia* is usually determined by passing several feet of the gas (measured by an experiment meter) slowly through a measured quantity of half normal sulphuric acid, and then by titration determining the amount of sulphuric acid which has been neutralized. A Peligot bulb tube, or a tube filled with marbles wetted with the sulphuric acid solution, may be used for the purpose—indeed, any method which permits the intimate contact of the gas with solution, and subsequent removal of the solution for titration. The ammonia ( $\text{NH}_3$ ) is calculated like the sulphur to grains per 100 ft. The amount found is usually in the neighborhood of two to three grains, though in certain cases it may run much higher.

## CHAPTER XLVI.

### SOAP.

A good hard soap should not contain less than 54 per cent of fat acids, combined with at least one eighth that amount of soda ( $\text{Na}_2\text{O}$ ), and not over 40 per cent of water.

In the analysis of soap, we may have to determine (1) *combined fatty acids*, (2) *unsaponified fat*, (3) *resin*, (4) *glycerine*, (5) *combined alkali* ( $\text{Na}_2\text{O}$ ), (6) *uncombined alkali* ( $\text{NaHO}$ ), (7) *free carbonate* ( $\text{Na}_2\text{CO}_3$ ), (8) *chloride*, *trace*, (9) *sulphate* ( $\text{Na}_2\text{SO}_4$ ), (10) *foreign matter*, which may include impurities or adulterants, as clay, sand, ochre, talc, sodium silicate, etc., and (11) *water*.

#### *Analysis.*

Dissolve 5 gms of the soap in fine shavings in 80 or 90 c. c. of 90 per cent alcohol, heating it on the water-bath until solution is effected.

The *solution* will then contain the first six constituents above-mentioned, together with the water, while the *residue* will contain the other constituents.

*Solution.*—Pass a current of carbon dioxide through it for some time. The uncombined alkali will be converted into  $\text{NaHCO}_3$ , and will precipitate. Filter, wash with alcohol, dissolve in water, and titre with half-normal sulphuric acid. (Alkalimetry p. 207.) Calculate to  $\text{NaHO}$  for (6) uncombined alkali.

To the filtrate or the alcoholic solution in which  $\text{CO}_2$  failed to produce a precipitate, add 15 or 20 c. c. of water, and evaporate off the alcohol. Add 25 or 30 c. c. of half-normal sulphuric acid from a burette, and a weighed quantity (5 gms.) of pure white wax, boil, filter through a wetted filter, and wash with boiling water until the washings are no longer acid. Cool the cake of wax which takes up the fat acids and resin, dry between bibulous

paper, and weigh. The weight, less the weight of the wax added, gives that of (1) combined fatty acids, (2) uncombined fat, and (3) resin.

In the filtrate from the wax, etc., determine by means of a half-normal soda solution, how much of the sulphuric acid used has been neutralized by the alkali of the soap, the result gives (5) combined alkali. Calculate to  $\text{Na}_2\text{O}$ .

*Residue.*—Dry and weigh, treat with water, and filter, dry again and weigh. The last weight is that of the (10) foreign matter insoluble in water. Titre the water solution with half-normal sulphuric acid. Calculate the result to  $\text{Na}_2\text{CO}_3$ . This gives (7) free carbonate. The first weight, less the foreign matter insoluble in water, and also less free carbonate, gives the weight of neutral salts soluble in water.

(2) *Uncombined Fat.*—Treat 5 gms. of the soap (cut into very fine shavings) with ether two or three times, pouring off the ether into a weighed dish. The operation may be assisted by placing the vessel over a water-bath containing hot water, but with no flame under it. Since the ether may dissolve small portions of the soap, it is safer to evaporate off the ether from the first extraction, and then to treat the residue again with ether. The weight of the residue left on the last evaporation of the ether gives (2) unsaponified fat. Carbon disulphide may be used in place of ether.

(3) *Resin.*—Dissolve 40 gms. of the soap in boiling water, add an excess of sulphuric acid to separate the fatty acids and resin, cool, pour off the aqueous portion, and digest the fatty residue with equal volumes of alcohol and water, agitating from time to time. Pour off the milky fluid, add more alcohol and water, and digest again. Repeat this until the fluid ceases to become milky, then add water and a weighed quantity of wax as before, filter, dry, and weigh the cake. The weight represents that of the fatty acids deprived of the resin. The difference of percentage obtained in this way from the percent-

age obtained as before described, gives approximately the amount of the resin present.

(4) *Glycerine*.—Dissolve 5 gms. of the soap in 90 per cent alcohol, add dilute alcoholic sulphuric acid (1 vol. concentrated sulphuric acid to 10 vols. alcohol) so long as a precipitate forms, filter, wash with alcohol, digest with barium carbonate and water until the alcohol is gone, filter, evaporate the filtrate to dryness in a weighed dish at gentle heat, and weigh the residue of *glycerine*.

(5, 6, 7, 8, 9, and 10) *Mineral Constituents*.—Calcine 5 gms., weigh, dissolve in water, filter. Residue is (10) foreign matter. Dilute the solution to some convenient bulk (say 200 c. c.). In one half, determine total alkali (5, 6, and 7) by titration with half-normal sulphuric acid. A portion may be taken to test for the presence of potassium salts. In one quarter, determine (8) chloride, by titration with standard solution of silver nitrate, with potassium chromate as indicator. In the remaining quarter, determine (9) sulphate, by precipitation with barium chloride, as usual. Calculate chloride and sulphate to NaCl and  $\text{Na}_2\text{SO}_4$ .

(11) *Water*.—Some analysts determine all the other constituents, and calculate the remainder as water. It may, however, be determined by dissolving 1 or 2 gms. in as little strong alcohol as possible, pouring the solution upon a weighed quantity of sand in a dish, and drying in the air-bath at  $110^\circ \text{C}$ . to constant weight. The loss represents the water.



## CHAPTER XLVII.

### FLOUR.

Digest 5 gms. of the flour in 100 c. c. cold water for one or two hours, with frequent stirring, filter through a filter previously exhausted with hydrochloric acid, washed, dried, and weighed, wash with about 100 c. c. cold water. The solution contains (1) *albumen*, (2) *gum*, (3) *sugar*, and a portion of the soluble salts. The residue contains (4) *cellulose*, (5) *starch*, *gluten*, and *fat*.

*Solution*.—1. Boil, and then filter; the precipitate consists of albumen. Dry at 100° C., and weigh.

[*Note*.—The treatment with water, filtration and precipitation of albumen should be completed on the same day. By keeping the solution hot it may be continued through two days, but this is not advisable.]

2. Evaporate the filtrate from the albumen nearly to dryness, add a large excess of alcohol, warm, and then allow it to cool, filter on a weighed filter, wash with alcohol. Dry at 100° C., and weigh the gum thus obtained.

3. Evaporate the alcoholic filtrate from the gum to small bulk, add water, and boil out the alcohol. Concentrate the solution to 50 c. c., and divide in halves. In the first half, determine the glucose direct by the copper sulphate solution as described under Raw Sugar (p. 225). In the second half, add a few drops of dilute sulphuric acid, boil, neutralize with potassium hydrate, and determine glucose by copper sulphate as before. The excess of glucose found in the second determination is due to cane sugar.

*Residue*.—Wash with a jet from the wash-bottle into a beaker. Then dry the filter with what adheres to it, and weigh. This weight, less that of the filter found at the beginning, gives the weight of adhering substance, which

must be taken into account in the subsequent determinations.

4. Add to the substance in the beaker, 50 times its weight of water containing one per cent of sulphuric acid, and heat for several hours, until the starch goes into solution, and only light flocculent cellulose is left. Filter and wash until all sulphuric acid is removed, dry at  $100^{\circ}$  C., and weigh.

5. To the filtrate from the cellulose, diluted to 400 c. c., add about 30 c. c. concentrated sulphuric acid, and heat on a water-bath at about  $95^{\circ}$  C. for several hours, adding water from time to time to keep it up to the original bulk. Digest thus until a drop of the solution shows no coloration when treated with diluted iodine solution, and also gives no precipitate with alcohol. When the conversion of the starch into glucose is complete, neutralize the excess of acid by sodium or potassium hydrate and determine the glucose with copper sulphate as before.

The starch can also be determined in a separate portion, by washing a weighed quantity with water, then with ether, and again with water, drying and then making an elementary analysis for carbon (see elementary analysis of sugar), or with copper oxide and lead chromate. The carbon found is from both starch and cellulose. Deduct the carbon due to cellulose found as above (formula,  $C_{12}H_{10}O_{10}$  the same as that of starch), and calculate the rest to starch (44 parts carbon = 100 parts starch).

*Albumenoids*.—Determine the total nitrogen in 1 gm. by combustion with soda-lime (guano, p. 222), and from this calculate the albumenoids; 15.5 parts N = 100 parts albumenoids. From this deduct the albumen found as above; the difference is gluten.

*Fat*.—Weigh out 2 or 3 gms. of the flour, treat with ether, boiling it gently over the water-bath, decant the ether through a filter into a weighed dish, repeat this two or three times, evaporate off the ether, and weigh the fat.

*Ash*.—Burn 40 or 50 gms. of the flour in a weighed dish.

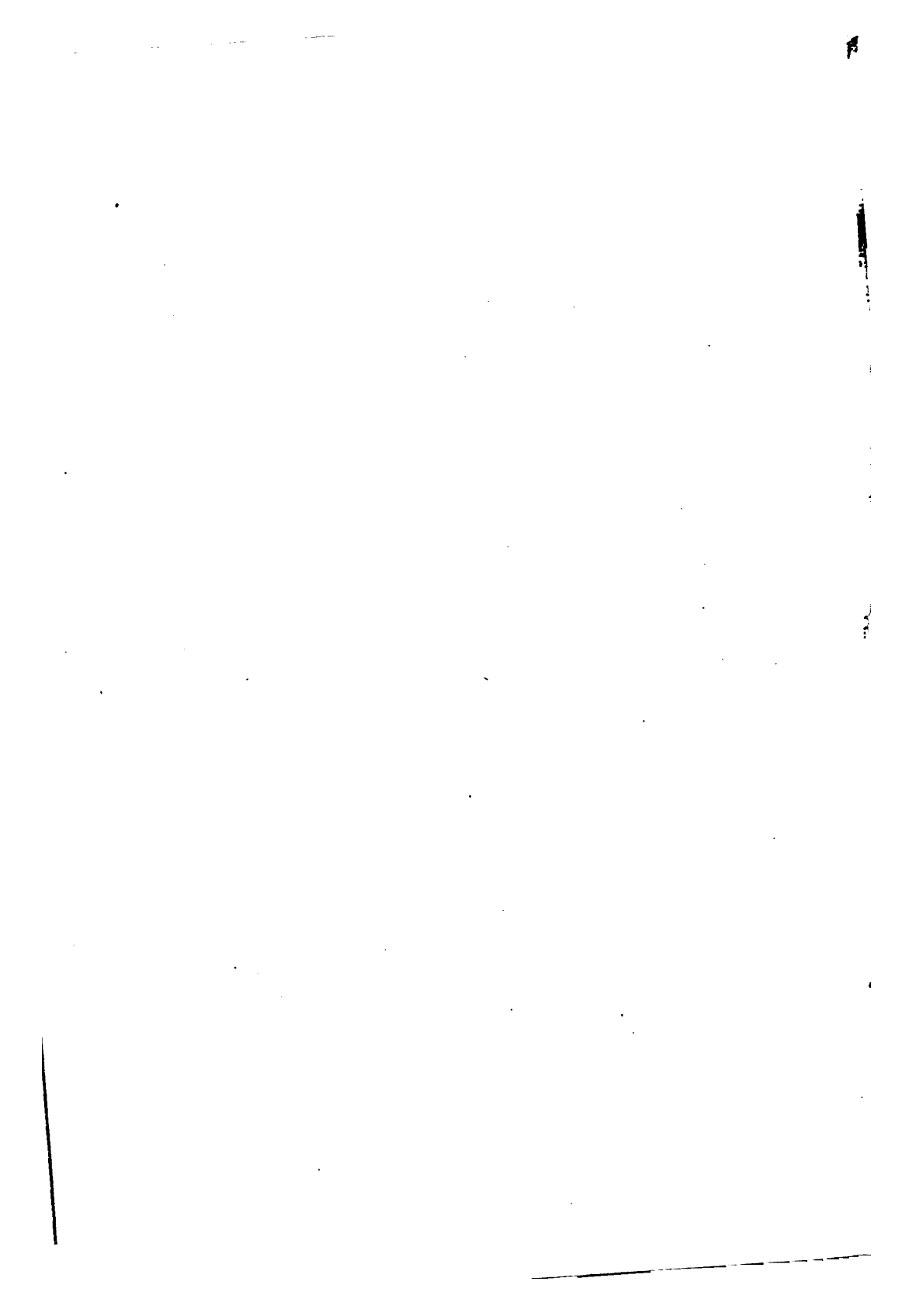
If there is any difficulty in burning off the carbon, cool and weigh the dish and contents ; then extract with hot water, filter through a small filter, avoiding any transfer of the carbonaceous substance to the filter. Dry the dish, and weigh again. The loss represents mineral salts dissolved out. Moisten with nitric acid, add the filter-paper and contents, and burn again, cool, and weigh. The weight, less that of the dish, represents the remainder of the ash. The weight of the ash of the small filter-paper may be ignored. The ash may be dissolved in water with a little nitric acid, and analyzed as required.

*Water.*—Dry 1 or 2 gms. in the air-bath at 110 to 120° C. to constant weight. Loss = water.

All filter-papers used in this analysis, on which different constituents (albumen, gum, etc.) are weighed, should be prepared by soaking for about half an hour in dilute hydrochloric acid (1 : 10) washing thoroughly with water, and drying.



# TABLES.



## TABLES OF WEIGHTS AND MEASURES.

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The following comparison of French weights and measures with those of the United States have been taken or calculated from similar tables given by Dr. Warren De la Rue. *Uré's Dictionary*, III., p. 1119.

Slight discrepancies from other authorities exist, *e. g.*, the gramme is given by De la Rue as equivalent to 15.4523 grains. The *U. S. Dispensatory*, 13th Ed., pp. 1734 and 1735, gives 15.434 grains, and refers to other authorities which give 15.444 grains as the equivalent of the gramme.

The number of grains in the U. S. gallon of 231 cubic inches is here taken as 58,318, which is believed to be correct, from a calculation based upon results obtained from experimental researches on the expansion of liquids, and a reference to the English standard for the wine or Winchester gallon, on which it is based. (See note of W. H. Chandler, *Am. Chem. I.*, 318.) The *U. S. Dispensatory* (*ib.*) gives 58,328.886 grains.

The report of F. R. Hassler, of the coast survey, gives 58,372.1754 in 1832, and in 1842 Hassler makes it 58,373 grains. The reasons for considering this erroneous will be found in Barnard's *Metric System*, p. 158.

## MEASURES OF CAPACITY (U. S. PHARMACOPEIA).

Gal.	Qts.	Pts.	Fl. oz.	Fl. dr.	Minims.	Grains of water at 62° F.	Cubic centimetres.
1	= 4	= 8	= 128	= 1,024	= 61,440	= 58,318.00	= 3,785.200
	1	2	32	256	15,360	14,579.50	946.300
		1	16	128	7,680	7,289.75	473.150
			1	8	480	455.61	29.570
				1	60	56.95	3.690
					1	0.95	0.061
1 English Imperial gallon	= 277.274 cu. in.					70,000.00	4,543.000
1 “ “ pint	= 34.659 “					8,750.00	568.000
<i>Other English gallons :</i>							
1 wine = Winchester gal.	= 231.000 “					58,318.00	3,785.200
1 corn gallon,	268.800 “					67,861.00	4,402.900
1 ale “	282.000 “					71,193.40	4,619.200
1 cu. ft. = 283.15 c. c.							
1 cu. in. = 16.38 c. c.						0.061027 cu. in. = 1 c. c.	

## LINEAR MEASURES.

	Metre.		Metre.
1 yard.....	0.91438	1 inch.....	0.0254
1 foot.....	0.30480	39.3708 inches.....	1.0000

## TROY WEIGHT.

Lb.	Oz.	Dwt.	Grs.	Grammes.
1	= 12	= 240	= 5,760	373.2419
	1	20	480	31.1035
		1	24	1.5552
			1	0.0648

## AVOIRDUPOIS WEIGHT.

Gross					Kilogrammes.
ton.	Cwt.	Qr.	St.	Lbs.	
1	= 20	= 80	= 160	= 2,240	1,016.00
	1	4	8	112	50.80
		1	2	28	12.70
			1	14	6.35
				Oz.	Dr.
				1	= 16
				1	16
					1

1 net ton = 2,000 lbs. .... 907 kilogrammes.

## APOTHECARIES' WEIGHT.

Lb.	Oz.	Dr.	Scruples.	Grains.	Grammes.
1	= 12	= 96	= 288	= 5,760	373.2419
	1	8	24	480	31.1035
		3	3	60	3.8879
			1	20	1.2960
0.0022 lb. Av.	= 0.03527 oz. Av. = 15.4323 grs.				1 gm.
				Lbs. Av.	Grammes.
1 cu. ft. water at 62° F.	= 62.3550				28,315.0000
1 cu. in. " " "	0.0361				16.8862

—Watts's Dictionary, V., 1010.

4 grains = 1 karat

1 gramme = 3.55 1/2 karats



# TABLE OF ATOMIC WEIGHTS.

Revised by C. F. CHANDLER and F. G. WIECHMANN,

OCTOBER, 1881.

Aluminium,	Al.	IV.	27.0	Manganese,	Mn.	VI.	55.0
Antimony,	Sb.	V.	120.0	Mercury,	Hg.	II.	200.0
Arsenic,	As.	V.	74.9	Molybdenum,	Mo.	VI.	96.0
Barium,	Ba.	II.	136.8	Nickel,	Ni.	VI.	59.0
Bismuth,	Bi.	V.	210.0	Nitrogen,	N.	V.	14.0
Boron,	B.	III.	11.0	Osmium,	Os.	II. IV.	199.0
Bromine,	Br.	I.	79.7	Oxygen,	O.	II.	16.0
Cadmium,	Cd.	II.	112.0	Palladium,	Pd.	IV.	106.0
Cæsium,	Cs.	I.	133.0	Phosphorus,	P.	V.	31.0
Calcium,	Ca.	II.	40.0	Platinum,	Pt.	IV.	197.0
Carbon,	C.	IV.	12.0	Potassium,	K.	I.	39.0
Cerium,	Ce.	III.	141.2	Rhodium,	Rh.	IV.	104.0
Chlorine,	Cl.	I.	35.4	Rubidium,	Rb.	I.	85.0
Chromium,	Cr.	VI.	52.4	Ruthenium,	Ru.	II. IV.	104.0
Cobalt,	Co.	VI.	59.0	Selenium,	Se.	II.	79.0
Columbium,	Cb.	V.	94.0	Silicon,	Si.	IV.	28.0
Copper,	Cu.	II.	63.1	Silver,	Ag.	I.	108.0
Davyum,	Da.		154.0	Sodium,	Na.	I.	23.0
Didymium,	D.	III.	147.0	Strontium,	Sr.	II.	87.5
Erbium,	E.	III.	169.0	Sulphur,	S.	II.	32.0
Fluorine,	F.	I.	19.0	Tantalum,	Ta.	V.	182.0
Gallium,	Ga.	III.	69.9	Tellurium,	Te.	II.	128.0
Glucium,	Gl.	II.	9.2	Thallium,	Tl.	I.	204.0
Gold,	Au.	III.	196.2	Thorium,	Th.	IV.	231.5
Hydrogen,	H.	I.	1.0	Tin,	Sn.	IV.	118.0
Indium,	In.	III.	113.4	Titanium,	Ti.	IV.	50.0
Iodine,	I.	I.	126.5	Tungsten,	W.	IV. VI.	184.0
Iridium,	Ir.	II.	198.0	Uranium,	U.	VI.	240.0
Iron,	Fe.	VI.	56.0	Vanadium,	V.	V.	51.2
Lanthanum,	La.	III.	139.0	Yttrium,	Y.	III.	60.0
Lead,	Pb.	II.	207.0	Zinc,	Zn.	II.	65.0
Lithium,	Li.	I.	7.0	Zirconium,	Zr.	IV.	90.0
Magnesium,	Mg.	II.	24.0				

NOTE.—The Artiads are printed in Roman, the Perissads in Italics.

TABLE OF SPECIFIC GRAVITIES CORRESPONDING WITH DEGREES BEAUMÉ FOR LIQUIDS LIGHTER THAN WATER.

The following is taken from the *United States Dispensatory* (Wood and Bache). In that volume three different values are given for the value of degrees Beaumé in specific gravities. Those which follow were from the French Codex :

Deg. B.	Specific gravity.	Deg. B.	Specific gravity.	Deg. B.	Specific gravity.	Deg. B.	Specific gravity.
10...	1.000	27...	0.894	44...	0.809	61...	0.738
11...	0.998	28...	0.889	45...	0.804	62...	0.735
12...	0.986	29...	0.883	46...	0.800	63...	0.731
13...	0.979	30...	0.878	47...	0.795	64...	0.727
14...	0.973	31...	0.872	48...	0.791	65...	0.724
15...	0.966	32...	0.867	49...	0.787	66...	0.720
16...	0.960	33...	0.862	50...	0.783	67...	0.716
17...	0.953	34...	0.857	51...	0.778	68...	0.713
18...	0.947	35...	0.852	52...	0.774	69...	0.709
19...	0.941	36...	0.847	53...	0.770	70...	0.706
20...	0.935	37...	0.842	54...	0.766	71...	0.702
21...	0.929	38...	0.837	55...	0.762	72...	0.699
22...	0.923	39...	0.832	56...	0.758	73...	0.696
23...	0.917	40...	0.827	57...	0.754	74...	0.692
24...	0.911	41...	0.823	58...	0.750	75...	0.689
25...	0.905	42...	0.818	59...	0.746	76...	0.686
26...	0.900	43...	0.813	60...	0.742	77...	0.682

The specific gravity may be calculated from the formula :

$$\text{Sp. gr.} = \frac{144}{B + 134} \quad B = \frac{144}{\text{Sp. gr.}} - 134$$

For specific gravities corresponding with degrees B. for liquids heavier than water, see Table of values of Sulphuric acid.

TABLE OF VALUES OF SULPHURIC ACID.

A. H. Elliott, *Proc. Am. Chem. Soc.*, II., p. 26, adopted by Manufacturing Chemists' Assoc. See Dingler, CCLIX., 268. Tables taken from Kolbe & Rosenstiehl's results. *Bulletin de la Soc. Ind. de Mulhouse*, July and August, 1872, pp. 209 and 238.

DEGREES BEAUMÉ.	Specific gravity.	Per cent H <sub>2</sub> SO <sub>4</sub> .	DEGREES BEAUMÉ.	Specific gravity.	Per cent H <sub>2</sub> SO <sub>4</sub> .
1.....	1.005	0.93	34.....	1.309	40.20
2.....	1.011	1.87	35.....	1.317	41.14
3.....	1.023	3.74	36.....	1.334	43.01
4.....	1.029	4.67	37.....	1.342	43.94
5.....	1.036	5.61	38.....	1.359	45.81
6.....	1.043	6.54	39.....	1.368	46.75
7.....	1.050	7.48	40.....	1.383	48.62
8.....	1.057	8.41	41.....	1.395	49.55
9.....	1.064	9.35	42.....	1.418	51.42
10.....	1.071	10.28	43.....	1.422	52.30
11.....	1.086	12.15	44.....	1.441	54.23
12.....	1.093	13.09	45.....	1.451	55.16
13.....	1.100	14.02	46.....	1.470	57.03
14.....	1.107	14.96	47.....	1.480	57.97
15.....	1.114	15.89	48.....	1.500	59.84
16.....	1.123	16.83	49.....	1.510	60.77
17.....	1.136	18.70	50.....	1.531	62.64
18.....	1.143	19.63	51.....	1.541	63.58
19.....	1.150	20.57	52.....	1.562	65.45
20.....	1.158	21.50	53.....	1.573	66.38
21.....	1.172	23.37	54.....	1.594	68.25
22.....	1.179	24.31	55.....	1.616	70.12
23.....	1.186	25.24	56.....	1.627	71.03
24.....	1.201	27.11	57.....	1.650	72.93
25.....	1.208	29.05	58.....	1.661	73.83
26.....	1.216	29.98	59.....	1.683	75.73
27.....	1.231	30.85	60.....	1.705	77.60
28.....	1.238	31.79	61.....	1.727	79.47
29.....	1.254	33.66	62.....	1.747	81.34
30.....	1.263	34.59	63.....	1.767	83.21
31.....	1.269	35.53	64.....	1.793	86.02
32.....	1.285	37.40	65.....	1.814	88.82
33.....	1.293	38.33	66.....	1.835	93.50

$$\text{Sp. gr.} = \frac{145}{145 - B^{\circ}}$$

$$B^{\circ} = 145 - \frac{145}{\text{Sp. gr.}}$$

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF HYDROCHLORIC ACID. TEMP.,  
15° (CER).

Specific gravity.	Per cent HCl.	Specific gravity.	Per cent HCl.	Specific gravity.	Per cent HCl.
1.2000	43.777	1.1328	23.913	1.0637	13.049
1.1982	40.369	1.1308	26.505	1.0617	12.641
1.1964	39.961	1.1287	26.098	1.0597	12.233
1.1946	39.554	1.1267	25.690	1.0577	11.825
1.1928	39.146	1.1247	25.282	1.0557	11.418
1.1910	38.738	1.12.6	24.874	1.0537	11.010
1.1893	38.330	1.1206	24.466	1.0517	10.602
1.1875	37.923	1.1185	24.058	1.0497	10.194
1.1857	37.516	1.1164	23.650	1.0477	9.786
1.1846	37.108	1.1143	23.242	1.0457	9.379
1.1822	36.700	1.1123	22.834	1.0437	8.971
1.1802	36.292	1.1102	22.426	1.0417	8.563
1.1782	35.884	1.1082	22.019	1.0397	8.155
1.1762	35.476	1.1061	21.611	1.0377	7.747
1.1741	35.068	1.1041	21.203	1.0357	7.340
1.1721	34.660	1.1020	20.796	1.0337	6.932
1.1701	34.252	1.1000	20.388	1.0318	6.524
1.1681	33.845	1.0980	19.980	1.0298	6.116
1.1661	33.437	1.0960	19.572	1.0279	5.709
1.1641	33.029	1.0939	19.165	1.0259	5.301
1.1620	32.621	1.0919	18.757	1.0239	4.893
1.1599	32.213	1.0899	18.349	1.0220	4.486
1.1578	31.805	1.0879	17.941	1.0200	4.078
1.1557	31.398	1.0857	17.534	1.0180	3.670
1.1537	30.990	1.0838	17.126	1.0160	3.262
1.1515	30.582	1.0818	16.718	1.0140	2.854
1.1494	30.174	1.0798	16.310	1.0120	2.447
1.1472	29.767	1.0778	15.902	1.0100	2.039
1.1452	29.359	1.0758	15.494	1.0080	1.631
1.1431	23.951	1.0738	15.087	1.0060	1.124
1.1410	28.544	1.0718	14.679	1.0040	0.816
1.1389	28.136	1.0697	14.271	1.0020	0.408
1.1369	27.728	1.0677	13.863		
1.1349	27.321	1.0657	13.456		

TABLE SHOWING THE AMOUNT OF NITRIC ACID ( $\text{HNO}_3$ ) CONTAINED IN SOLUTIONS OF DIFFERENT SPECIFIC GRAVITIES. TEMP.,  $15^\circ$  (URE).

$\text{HNO}_3$ per cent.	Specific gravity.	$\text{HNO}_3$ per cent.	Specific gravity.	$\text{HNO}_3$ per cent.	Specific gravity.
100.....	1.5000	63.....	1.3783	33.....	1.1895
99.....	1.4980	65.....	1.3732	32.....	1.1833
98.....	1.4960	64.....	1.3681	31.....	1.1770
97.....	1.4940	63.....	1.3630	30.....	1.1709
96.....	1.4910	62.....	1.3579	29.....	1.1648
95.....	1.4880	61.....	1.3529	28.....	1.1587
94.....	1.4850	60.....	1.3477	27.....	1.1526
93.....	1.4820	59.....	1.3427	26.....	1.1465
92.....	1.4790	58.....	1.3376	25.....	1.1403
91.....	1.4760	57.....	1.3323	24.....	1.1345
90.....	1.4730	56.....	1.3270	23.....	1.1286
89.....	1.4700	55.....	1.3216	22.....	1.1227
88.....	1.4670	54.....	1.3163	21.....	1.1168
87.....	1.4640	53.....	1.3110	20.....	1.1109
86.....	1.4600	52.....	1.3056	19.....	1.1051
85.....	1.4570	51.....	1.3001	18.....	1.0993
84.....	1.4530	50.....	1.2947	17.....	1.0935
83.....	1.4500	49.....	1.2887	16.....	1.0878
82.....	1.4460	48.....	1.2826	15.....	1.0821
81.....	1.4424	47.....	1.2765	14.....	1.0764
80.....	1.4385	46.....	1.2705	13.....	1.0703
79.....	1.4346	45.....	1.2644	12.....	1.0651
78.....	1.4306	44.....	1.2583	11.....	1.0595
77.....	1.4269	43.....	1.2523	10.....	1.0540
76.....	1.4228	42.....	1.2462	9.....	1.0485
75.....	1.4189	41.....	1.2402	8.....	1.0430
74.....	1.4147	40.....	1.2341	7.....	1.0375
73.....	1.4107	39.....	1.2277	6.....	1.0320
72.....	1.4065	38.....	1.2212	5.....	1.0267
71.....	1.4023	37.....	1.2148	4.....	1.0212
70.....	1.3978	36.....	1.2084	3.....	1.0159
69.....	1.3945	35.....	1.2019	2.....	1.0106
68.....	1.3882	34.....	1.1958	1.....	1.0053
67.....	1.3833				

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF CRYSTALLIZED TARTARIC ACID IN WATER. TEMP., 15°. WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SALZLÖSUNGEN."					
Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00450	20.....	1.09698	39.....	1.20190
2.....	1.00900	21.....	1.10200	40.....	1.20785
3.....	1.01360	22.....	1.10720	41.....	1.21380
4.....	1.01790	23.....	1.11240	42.....	1.21980
5.....	1.02240	24.....	1.11750	43.....	1.22590
6.....	1.02730	25.....	1.12270	44.....	1.23170
7.....	1.03220	26.....	1.12820	45.....	1.23770
8.....	1.03710	27.....	1.13380	46.....	1.24410
9.....	1.04200	28.....	1.13930	47.....	1.25040
10.....	1.04692	29.....	1.14490	48.....	1.25680
11.....	1.05170	30.....	1.15047	49.....	1.26320
12.....	1.05650	31.....	1.15600	50.....	1.26962
13.....	1.06130	32.....	1.16150	51.....	1.27620
14.....	1.06620	33.....	1.16700	52.....	1.28280
15.....	1.07090	34.....	1.17260	53.....	1.28940
16.....	1.07610	35.....	1.17810	54.....	1.29610
17.....	1.08130	36.....	1.18400	55.....	1.30270
18.....	1.08650	37.....	1.19000	56.....	1.30930
19.....	1.09170	38.....	1.19590	57.....	1.31590

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF CRYSTALLIZED CITRIC ACID IN WATER. TEMP., 15°. WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SALZLÖSUNGEN."					
Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00370	23.....	1.09300	45.....	1.19470
2.....	1.00740	24.....	1.09720	46.....	1.19980
3.....	1.01110	25.....	1.10140	47.....	1.20500
4.....	1.01490	26.....	1.10600	48.....	1.21030
5.....	1.01860	27.....	1.11060	49.....	1.21530
6.....	1.02270	28.....	1.11520	50.....	1.22041
7.....	1.02680	29.....	1.11980	51.....	1.22570
8.....	1.03090	30.....	1.12439	52.....	1.23170
9.....	1.03500	31.....	1.12880	53.....	1.23590
10.....	1.03916	32.....	1.13330	54.....	1.24100
11.....	1.04310	33.....	1.13780	55.....	1.24620
12.....	1.04700	34.....	1.14220	56.....	1.25140
13.....	1.05090	35.....	1.14670	57.....	1.25720
14.....	1.05490	36.....	1.15150	58.....	1.26270
15.....	1.05800	37.....	1.15640	59.....	1.26830
16.....	1.06320	38.....	1.16120	60.....	1.27322
17.....	1.06750	39.....	1.16610	61.....	1.27940
18.....	1.07180	40.....	1.17093	62.....	1.28490
19.....	1.07620	41.....	1.17560	63.....	1.29040
20.....	1.08052	42.....	1.18140	64.....	1.29600
21.....	1.08480	43.....	1.18510	65.....	1.30150
22.....	1.08890	44.....	1.18990	66.....	1.30710

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF ACETIC ACID. TEMP., 15°.

$C_2H_4O_2$ per cent.	Specific gravity.	$C_2H_4O_2$ per cent.	Specific gravity.	$C_2H_4O_2$ per cent.	Specific gravity.	$C_2H_4O_2$ per cent.	Specific gravity.
0...	1.0000	26..	1.0363	51..	1.0623	76..	1.0747
1...	1.0007	27..	1.0375	52..	1.0631	77..	1.0748
2...	1.0022	28..	1.0388	53..	1.0638	78..	1.0748
3...	1.0037	29..	1.0400	54..	1.0646	79..	1.0748
4...	1.0052	30..	1.0412	55..	1.0653	80..	1.0748
5...	1.0067	31..	1.0424	56..	1.0660	81..	1.0747
6...	1.0083	32..	1.0436	57..	1.0666	82..	1.0746
7...	1.0098	33..	1.0447	58..	1.0673	83..	1.0744
8...	1.0113	34..	1.0459	59..	1.0679	84..	1.0742
9...	1.0127	35..	1.0470	60..	1.0685	85..	1.0739
10...	1.0142	36..	1.0481	61..	1.0691	86..	1.0736
11...	1.0157	37..	1.0492	62..	1.0697	87..	1.0731
12...	1.0171	38..	1.0502	63..	1.0702	88..	1.0726
13...	1.0185	39..	1.0513	64..	1.0707	89..	1.0720
14...	1.0201	40..	1.0523	65..	1.0712	90..	1.0713
15...	1.0214	41..	1.0533	66..	1.0717	91..	1.0705
16...	1.0228	42..	1.0543	67..	1.0721	92..	1.0696
17...	1.0242	43..	1.0552	68..	1.0725	93..	1.0686
18...	1.0256	44..	1.0562	69..	1.0729	94..	1.0674
19...	1.0270	45..	1.0571	70..	1.0733	95..	1.0660
20...	1.0284	46..	1.0580	71..	1.0737	96..	1.0644
21...	1.0298	47..	1.0589	72..	1.0740	97..	1.0625
22...	1.0311	48..	1.0598	73..	1.0742	98..	1.0604
23...	1.0324	49..	1.0607	74..	1.0744	99..	1.0580
24...	1.0337	50..	1.0615	75..	1.0746	100..	1.0553
25...	1.0350						

TABLE SHOWING THE PERCENTAGE OF AMMONIA ( $NH_3$ ) CONTAINED IN SOLUTIONS OF DIFFERENT SPECIFIC GRAVITIES. TEMP., 14° (CARIUS).

Specific gravity.	Ammonia, per cent.	Specific gravity.	Ammonia, per cent.	Specific gravity.	Ammonia, per cent.	Specific gravity.	Ammonia, per cent.
0.8844	36	0.9052	27	0.9314	18	0.9631	9
0.8864	35	0.9078	26	0.9347	17	0.9670	8
0.8885	34	0.9106	25	0.9380	16	0.9709	7
0.8907	33	0.9133	24	0.9414	15	0.9749	6
0.8929	32	0.9162	23	0.9449	14	0.9790	5
0.8953	31	0.9191	22	0.9484	13	0.9831	4
0.8976	30	0.9221	21	0.9520	12	0.9873	3
0.9001	29	0.9251	20	0.9556	11	0.9915	2
0.9026	28	0.9283	19	0.9593	10	0.9959	1

TABLE SHOWING THE AMOUNT OF  $K_2O$  IN POTASSA LYE OF DIFFERENT SPECIFIC GRAVITIES. TEMP.,  $17.5^\circ$ .

HOFFMAN, SCHAEGLER, "TABELLEN FÜR CHEMIKER," P. 119.

$K_2O$ per cent.	Specific gravity.	$K_2O$ per cent.	Specific gravity.	$K_2O$ per cent.	Specific gravity.	$K_2O$ per cent.	Specific gravity.
45.	1.576	34.	1.414	23.	1.239	12.	1.135
44.5	1.568	33.5	1.407	22.5	1.263	11.5	1.129
44.	1.560	33.	1.400	22.	1.257	11.	1.123
43.5	1.553	32.5	1.393	21.5	1.250	10.5	1.117
43.	1.545	32.	1.386	21.	1.244	10.	1.111
42.5	1.537	31.5	1.379	20.5	1.238	9.5	1.105
42.	1.530	31.	1.372	20.	1.231	9.	1.099
41.5	1.522	30.5	1.365	19.5	1.225	8.5	1.094
41.	1.514	30.	1.358	19.	1.219	8.	1.088
40.5	1.507	29.5	1.352	18.5	1.213	7.5	1.082
40.	1.500	29.	1.345	18.	1.207	7.	1.076
39.5	1.492	28.5	1.339	17.5	1.201	6.5	1.070
39.	1.484	28.	1.332	17.	1.195	6.	1.065
38.5	1.477	27.5	1.326	16.5	1.189	5.5	1.059
38.	1.470	27.	1.320	16.	1.183	5.	1.054
37.5	1.463	26.5	1.313	15.5	1.177	4.5	1.048
37.	1.456	26.	1.307	15.	1.171	4.	1.042
36.5	1.449	25.5	1.301	14.5	1.165	3.5	1.037
36.	1.442	25.	1.294	14.	1.159	3.	1.031
35.5	1.435	24.5	1.288	13.5	1.153	2.5	1.026
35.	1.428	24.	1.282	13.	1.147	2.	1.021
34.5	1.421	23.5	1.275	12.5	1.141	1.5	1.015

TABLE SHOWING THE SODIUM OXIDE ( $Na_2O$ ) IN SODA LYES OF DIFFERENT SPECIFIC GRAVITIES. TEMP.,  $17.5^\circ$ .

HOFFMAN-SCHAEGLER, "TABELLEN FÜR CHEMIKER."

$Na_2O$ per cent.	Specific gravity.	$Na_2O$ per cent.	Specific gravity.	$Na_2O$ per cent.	Specific gravity.	$Na_2O$ per cent.	Specific gravity.
35.	1.500	27.5	1.389	20.	1.231	12.5	1.174
34.5	1.492	27.	1.382	19.5	1.274	12.	1.167
34.	1.485	26.5	1.375	19.	1.266	11.5	1.160
33.5	1.477	26.	1.367	18.5	1.259	11.	1.153
33.	1.470	25.5	1.360	18.	1.252	10.5	1.146
32.5	1.463	25.	1.353	17.5	1.245	10.	1.139
32.	1.455	24.5	1.345	17.	1.238	9.5	1.132
31.5	1.448	24.	1.338	16.5	1.231	9.	1.125
31.	1.440	23.5	1.331	16.	1.224	8.5	1.118
30.5	1.433	23.	1.324	15.5	1.217	8.	1.111
30.	1.426	22.5	1.317	15.	1.210	7.5	1.104
29.5	1.418	22.	1.309	14.5	1.203	7.	1.097
29.	1.411	21.5	1.302	14.	1.195	6.5	1.090
28.5	1.404	21.	1.295	13.5	1.188	6.	1.083
28.	1.396	20.5	1.288	13.	1.181	5.5	1.076



TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF SODIUM CHLORIDE AT 15°.  
WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SALZLÖSUNGEN."			
Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00725	14.....	1.10884
2.....	1.01450	15.....	1.11146
3.....	1.02174	16.....	1.11988
4.....	1.02899	17.....	1.12790
5.....	1.03624	18.....	1.13523
6.....	1.04366	19.....	1.14315
7.....	1.05108	20.....	1.15107
8.....	1.05851	21.....	1.15931
9.....	1.06593	22.....	1.16755
10.....	1.07335	23.....	1.17580
11.....	1.08097	24.....	1.18404
12.....	1.08859	25.....	1.19228
13.....	1.09622	26.....	1.20098

TABLE SHOWING THE PERCENTAGE OF AMMONIUM CHLORIDE IN SOLUTIONS  
OF DIFFERENT SPECIFIC GRAVITIES. TEMP., 15°. WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SALZLÖSUNGEN."			
Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00816	14.....	1.04925
2.....	1.00632	15.....	1.04524
3.....	1.00948	16.....	1.04805
4.....	1.01264	17.....	1.05086
5.....	1.01580	18.....	1.05367
6.....	1.01880	19.....	1.05648
7.....	1.02180	20.....	1.05929
8.....	1.02481	21.....	1.06204
9.....	1.02781	22.....	1.06479
10.....	1.03081	23.....	1.06754
11.....	1.03370	24.....	1.07029
12.....	1.03658	25.....	1.07304
13.....	1.03947	26.....	1.07575



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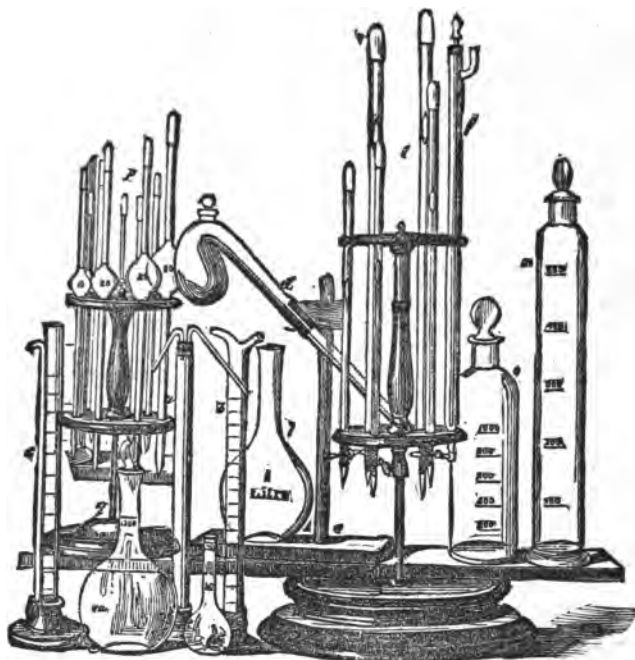
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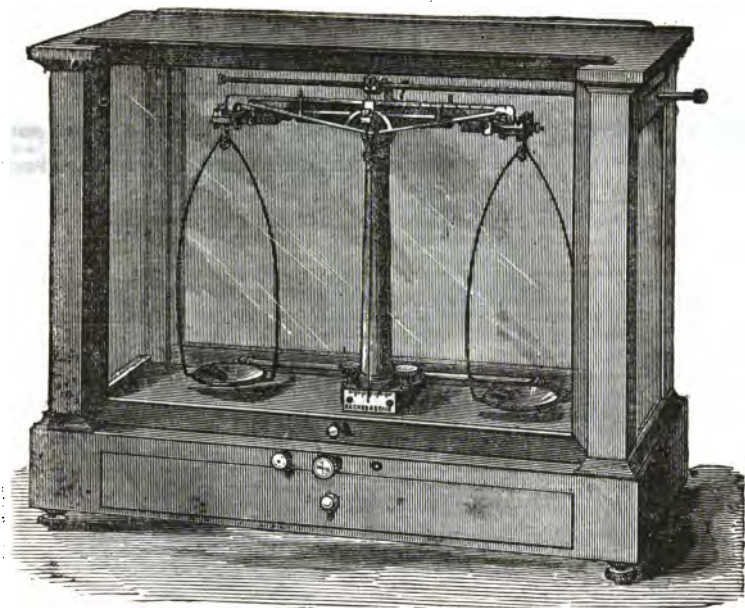
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